Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

SUPPORTING INFORMATION

Gold(I)-Catalyzed Diastereo- and Enantioselective [4+3] Cycloadditions: Construction of Functionalized Furano-benzoxepins

Xunhua Wang, Ruifeng Lv, and Xiaoxun Li*

Department of Medicinal Chemistry, Key Laboratory of Chemical Biology (Ministry of Education) and NMPA Key Laboratory for Technology Research and Evaluation of Drug Products, School of Pharmaceutical Sciences, Cheeloo College of Medicine, Shandong University, Jinan, Shandong, 250012, China.

Suzhou Research Institute, Shandong University, Suzhou, Jiangsu 215123, China

*Correspondence to: xli@sdu.edu.cn.

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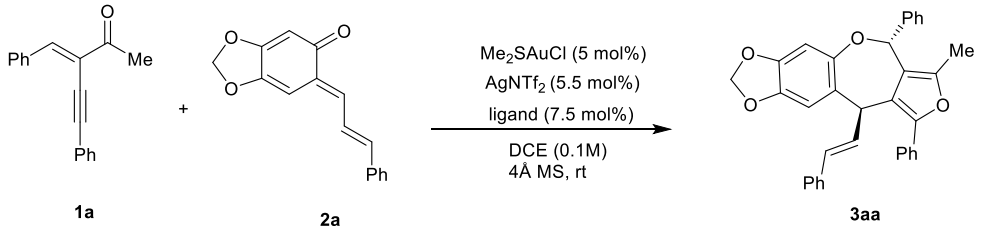
1. General Information

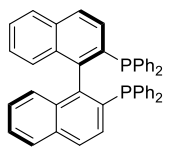
Unless otherwise noted, all the reactions for the preparation of the substrates were performed in oven-dried glassware under nitrogen atmosphere with freshly distilled solvents. The catalytic reactions were performed under nitrogen atmosphere. The solvents were purified by distillation from calcium hydride unless otherwise noted. All other commercial reagents were used without further purification unless otherwise indicated. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400 MHz spectrometer (ADVNCE III) using chloroform-*d* ($CDCl_3$) and dimethyl sulphoxide-*d6* (DMSO- *d6*) as the internal standard. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.10) or tetramethylsilane (TMS δ 0.00) was used as a reference. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. The enantiomeric excesses (e.e.) was determined by HPLC analysis on LC-20AD/T LPGE KIT using Daicel CHIRALPAK® column IA-3. X-ray diffraction analyses were carried out on a microcrystalline powder using a Rigaku Oxford Diffraction XtaLAB Synergy-S diffractometer using Cu radiation (λ = 1.54184 Å). If not specially mentioned, flash column chromatography was performed using 200-300 silica gel purchased from Yantai Chemicals (China). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization) as ionization method. Optical rotations were recorded on an AUTOPOL II digital polarimeter at 589 nm and are recorded as $[\alpha]_D^T$ (concentration in grams/100 mL solvent). The 2-(1-alkynyl)-2-alken-1-ones [1-2] and *ortho*-quinone methides [3-4] were prepared according to the reported procedures.

2. Reaction Optimization

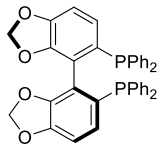
Table S1. Investigation of chiral ligands



1a 2a 3aa



L1



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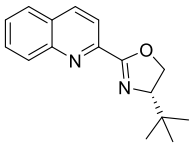

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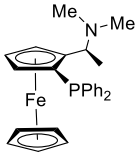

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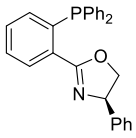

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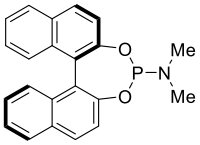

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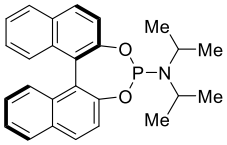

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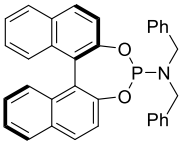

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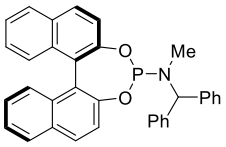

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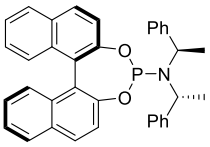

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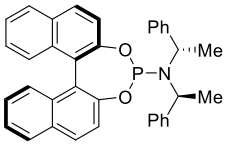

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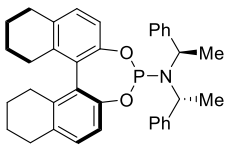

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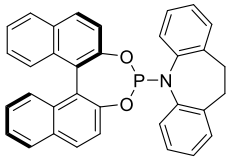

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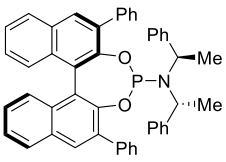

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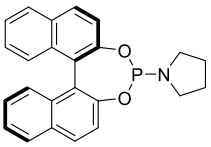

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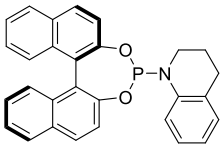


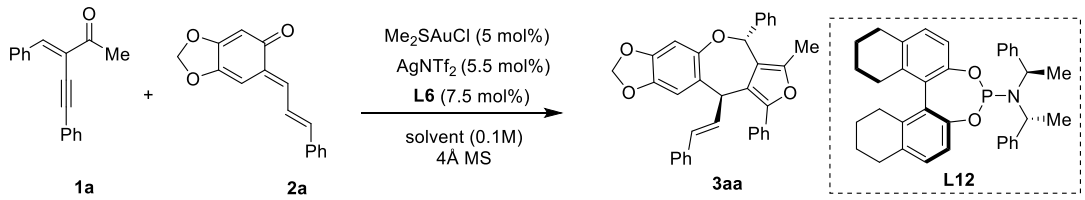
L16

Entry	Ligand	Yield[b]	ee[c]
1	L1	trace	--
2	L2	trace	--
3	L3	NR	--
4	L4	33%	21%
5	L5	58%	7%
6	L6	88%	57%
7	L7	74%	75%
8	L8	65%	60%
9	L9	49%	29%
10	L10	76%	77%
11	L11	78%	85%
12	L12	80%	93%
13	L13	56%	27%
14	L14	trace	--
15	L15	48%	19%
16	L16	65%	55%

[a] Unless otherwise indicated, all reactions were performed with **1a** (0.1 mmol) and **2a** (0.13 mmol) in the presence of Me_2SAuCl (5 mol%), ligand (7.5 mol%), $AgNTf_2$ (5.5 mol%) in DCE (1.0 mL) at room temperature under nitrogen atmosphere. [b] Isolated yield of product **3aa**. [c] Determined by HPLC analysis.

After optimization, **L12** was selected for the next investigation.

Table S2. Investigation of solvents and temperature

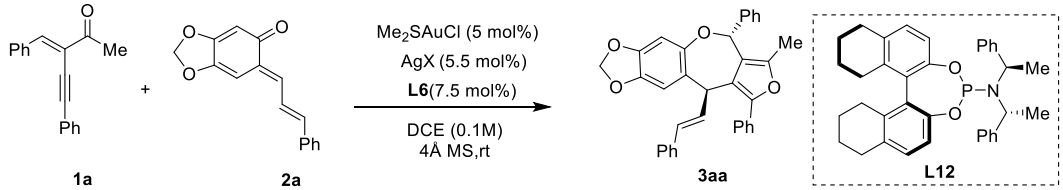


Entry	Temperature	Solvent	Yield[b]	ee[c]
1	rt	THF	trace	--
2	rt	DCM	70%	93%
3	rt	toluene	35%	90%
4	rt	$CHCl_3$	75%	92%
5	rt	MeCN	trace	--
6	10 ºC	DCE	75%	93%
7	0 ºC	DCE	64%	93%
8	-10 ºC	DCE	32%	94%

Unless otherwise indicated, all reactions were performed with **1a** (0.1 mmol) and **2a** (0.13 mmol) in the presence of Me_2SAuCl (5 mol%), **L12** (7.5 mol%), $AgNTf_2$ (5.5 mol%) in solvent (1.0 mL) at room temperature or 10 ºC or 0 ºC or -10 ºC under nitrogen atmosphere. [b] Isolated yield of product **3aa**. [c] Determined by HPLC analysis.

After optimization, the reaction with DCE as solvent at room temperature showed the optimal result.

Table S3. Investigation of silver salts

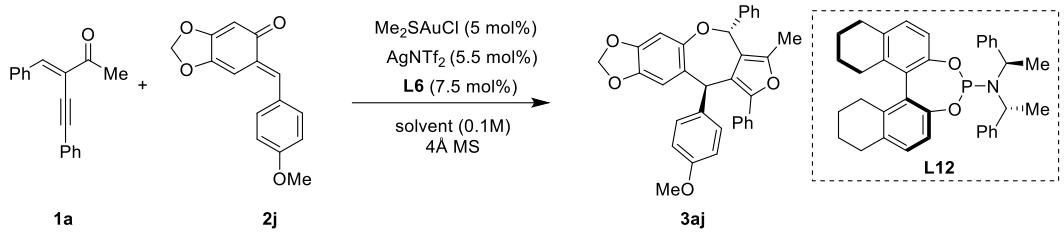


Entry	AgX	Yield [b]	ee [c]
1	AgOTf	51%	92%
2	$AgNTf_2$	80%	93%
3	$AgBF_4$	43%	93%
4	$AgPF_6$	60%	93%
5	$AgSbF_6$	81%	92%

[a] Unless otherwise indicated, all reactions were performed with **1a** (0.1 mmol) and **2a** (0.13 mmol) in the presence of Me_2SAuCl (5 mol%), **L12** (7.5 mol%), AgX (5.5 mol%) in DCE (1.0 mL) at room temperature under nitrogen atmosphere. [b] Isolated yield of product **3aa**. [c] Determined by HPLC analysis.

After optimization, the reaction with $AgNTf_2$ showed the best result.

Table S4. Investigation of solvents and temperature



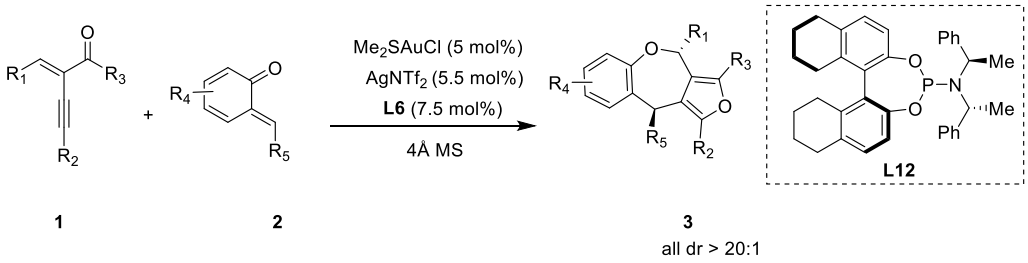
1a 2j 3aj

Entry	Temperature	Solvent	Yield[b]	ee[c]
1	rt	DCE	75%	77%
2	0 ºC	DCE	71%	80%
3	-10 ºC	DCE	55%	82%
4	-10 ºC	DCM	75%	86%
5	-10 ºC	$CHCl_3$	65%	88%
6	-10 ºC	TCE	72%	86%
7	-10 ºC	PhCl	80%	83%
9	-10 ºC	PhF	74%	90%
10	-10 ºC	$PhCl_2$	72%	88%
11	-20 ºC	PhF	76%	92%
12	-30 ºC	PhF	66%	92%

Unless otherwise indicated, all reactions were performed with **1a** (0.1 mmol) and **2j** (0.13 mmol) in the presence of Me_2SAuCl (5 mol%), **L12** (7.5 mol%), $AgNTf_2$ (5.5 mol%) in solvent (1.0 mL) under nitrogen atmosphere. [b] Isolated yield of product **3aj**. [c] Determined by HPLC analysis.

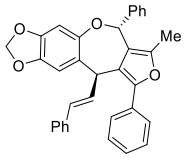
After optimization, the best reaction condition was with the PhF at -20ºC, which was selected as the standard condition.

3. Representative procedure and data for the synthesis of 3



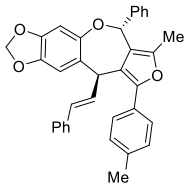
General procedure 1: Under nitrogen atmosphere, a solution of **L12** (7.5 mol%) and Me_2SAuCl (5 mol%) in DCE (0.5 mL) was stirred at room temperature for 2 h, then the solvent was removed in vacuum. Next, $AgNTf_2$ (5.5 mol%) and DCE (0.5 mL) was added to the residue, and the mixture was stirred at room temperature for 15 min. Then the precipitate was removed and the remaining solution was transferred into a solution of ketone substrate **1** (0.1 mmol, 1.0 equiv.) and *ortho* quinone methides **2** (0.13 mmol, 1.3 equiv.) with 4 Å molecular sieves 300 mg in DCE (0.5 mL) at room temperature. Once the reaction was complete as indicated by TLC, the solvent was removed under reduced pressure, and the residue was purified by a silica gel column using ethyl acetate/ petroleum ether (1/60-1/4) as the eluent to give product **3**.

General procedure 2: Under nitrogen atmosphere, a solution of **L12** (7.5 mol%) and Me_2SAuCl (5 mol%) in DCE (0.5 mL) was stirred at room temperature for 2 h, then the solvent was removed in vacuum. Next, $AgNTf_2$ (5.5 mol%) and PhF (0.5 mL) was added to the residue, and the mixture was stirred at room temperature for 15 min. Then the precipitate was removed and the remaining solution was transferred into a solution of ketone substrate **1** (0.1 mmol, 1.0 equiv.) and *ortho* quinone methides **2** (0.13 mmol, 1.3 equiv.) with 4 Å molecular sieves 300 mg in PhF (0.5 mL) at -20 ºC. Once the reaction was complete as indicated by TLC, the solvent was removed under reduced pressure, and the residue was purified by a silica gel column using ethyl acetate/ petroleum ether (1/40-1/4) as the eluent to give product **3**.



(6R,10S)-7-methyl-6,9-diphenyl-10-((E)-styryl)-6H,10H [1,3] dioxolo[4',5':4,5] benzo[1,2-b] furo[3,4-e] oxepine (3aa)

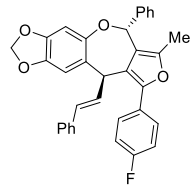
According to general procedure 1: White solid, m.p. = 96-98 ℃, 40 mg; 80% yield; 93% ee; $[\alpha]_D^{20.0}$ = -8.0 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm ×25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =9.3 min, t (minor) =7.4 min]; ^{1}H NMR (400 MHz, $CDCl_3$); δ 1.81 (s, 3H), 4.67 (d, *J* = 5.9 Hz, 1H), 5.68 (s, 1H), 5.77 (s, 2H), 6.34 (s, 1H), 6.49 (d, *J* = 15.9 Hz, 1H), 6.65 (s, 1H), 6.82 (dd, *J* = 5.9, 15.9 Hz, 1H), 7.09 (d, *J* = 6.1 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.22-7.30 (m, 5H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 44.8, 78.7, 101.2, 107.2, 108.3, 119.9, 120.4, 126.3, 126.5, 127.2, 127.3, 128.2, 128.5, 128.6, 128.8, 129.4, 129.5, 130.2, 131.3, 132.2, 137.4, 138.9, 143.9, 146.3, 147.0, 147.1, 147.6; HRMS (ESI) m/z calcd. for $C_{34}H_{27}O_4$ $[M+H]^+$: 499.1904, found: 499.1901.



(6R,10S)-6,9-diphenyl-10-((E)-styryl)-7-(p-tolyl)-6H,10H-[1,3]dioxolo [4',5':4,5] benzo[1,2-b] furo [3,4-e] oxepine (3ba)

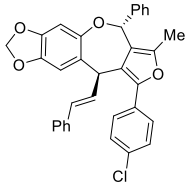
According to general procedure 1: White solid, m.p. = 90-92 ℃, 45 mg; 88% yield; 90% ee; $[\alpha]_D^{20.0}$ = -1.0 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm×25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =9.6 min, t (minor) =6.9 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.80 (s, 3H), 2.39 (s, 3H), 4.64 (d, *J* = 5.8 Hz, 1H), 5.68 (s, 1H), 5.77 (s, 2H), 6.33 (s, 1H), 6.48 (d, *J* = 15.9 Hz, 1H), 6.64 (s, 1H), 6.82 (dd, *J* = 5.9, 15.9 Hz, 1H), 7.10 (d, *J* = 6.1 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.22-7.29 (m, 7H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.54 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 21.4, 44.8, 78.8, 101.2, 107.2, 108.3, 119.8, 126.3, 126.5, 127.2, 128.1, 128.2, 128.4, 128.5, 128.6, 129.4, 129.5, 129.6, 130.3, 132.4, 137.2, 137.5, 138.9, 143.9,

146.3, 146.7, 147.2, 147.7; HRMS (ESI) m/z calcd. for $C_{35}H_{29}O_4$ $[M+H]^+$: 513.2060, found: 513.2052.



(6R,10S)-7-(4-fluorophenyl)-6,9-diphenyl-10-((E)-styryl)-6H,10H-[1,3]dioxolo [4',5':4,5] benzo[1,2-b] furo[3,4-e] oxepine (3ca)

According to general procedure 1: White solid, m.p. = 100-102 ℃; 42 mg, 81% yield; 92% ee; $[\alpha]_D^{20.0}$ = -15.9 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm ×25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =9.9 min, t (minor) =7.3 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.80 (s, 3H), 4.58 (s, 1H), 5.68 (s, 1H), 5.78 (s, 2H), 6.33 (s, 1H), 6.47 (d, *J* = 15.9 Hz, 1H), 6.64 (s, 1H), 6.80 (dd, *J* = 6.0, 15.9 Hz, 1H), 7.07-7.21 (m, 5H), 7.23-7.32 (m, 5H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.61 (dd, *J* = 5.4, 8.6 Hz, 2H);^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 44.9, 78.7, 101.2, 107.2, 108.2, 115.8 (d, *J* = 21.6 Hz), 120.0, 120.1, 126.6, 127.3, 127.5 (d, *J* = 3.3 Hz), 128.1, 128.2, 128.5, 128.7, 129.5, 129.6, 130.0, 132.1, 137.3, 138.8, 144.0, 146.2, 146.4, 147.1, 147.7, 162.2 (d, *J* = 247.3 Hz); HRMS (ESI) m/z calcd. for $C_{34}H_{26}FO_4$ $[M+H]^+$:517.1810, found: 517.1802.

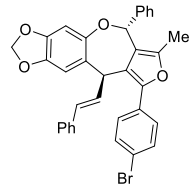


(6R,10S)-9-(4-chlorophenyl)-7-methyl-6-phenyl-10-((E)-styryl)-6H,10H- [1,3] Dioxolo [4',5':4,5] benzo[1,2-b] furo[3,4-e] oxepine (3da)

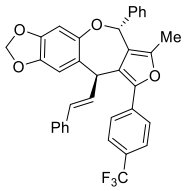
According to general procedure 1: White solid, m.p. = 140-142 ℃; 33 mg, 62% yield; 91% ee; $[\alpha]_D^{20.0}$ = 0.8 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm×25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =10.7 min, t (minor) =7.3 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81 (s, 3H), 4.59 (d, *J* = 5.3 Hz, 1H), 5.67 (s, 1H), 5.79 (s, 2H), 6.33 (s, 1H), 6.46 (d, *J* = 15.8 Hz, 1H), 6.64 (s, 1H), 6.79 (dd, *J* = 6.0, 15.9 Hz, 1H), 7.09 (d, *J* = 6.4 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.23-7.32 (m, 5H),

7.39 (dd, *J* = 8.1, 11.7 Hz, 4H), 7.58 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 12.9, 44.9, 78.7, 101.3, 107.2, 108.2, 120.2, 120.9, 126.6, 127.3, 127.5, 128.2, 128.5, 128.7, 129.0, 129.5, 129.7, 129.8, 130.0, 131.9, 133.1, 137.3, 138.7, 144.0, 146.0, 146.4, 147.5, 147.6; HRMS (ESI) m/z calcd. for $C_{34}H_{26}ClO_4$ $[M+H]^+$: 533.1514, found: 533.1512.

(6R,10S)-9-(4-bromophenyl)-7-methyl-6-phenyl-10-((E)-styryl)-6H,10H-[1,3] dioxolo [4',5':4,5] benzo[1,2-b] furo[3,4-e] oxepine (3ea)



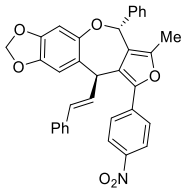
According to general procedure 1: Yellow solid, m.p. = 110-112 ℃; 50 mg, 86% yield; 93% ee; $[\alpha]_D^{20.0}$ = -0.6 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm ×25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =11.7 min, t (minor) =7.8 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 1.80 (s, 3H), 4.59 (d, *J* = 5.6 Hz, 1H), 5.67 (s, 1H), 5.78 (s, 2H), 6.33 (s, 1H), 6.46 (d, *J* = 15.9 Hz, 1H), 6.64 (s, 1H), 6.79 (dd, *J* = 6.0, 15.9 Hz, 1H), 7.08 (d, *J* = 6.3 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.22-7.31 (m, 5H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.48-7.58 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 12.9, 44.9, 78.6, 101.2, 107.2, 108.2, 120.2, 121.0, 121.2, 126.5, 127.3, 127.7, 128.2, 128.5, 128.7, 129.4, 129.7, 129.9, 130.1, 131.8, 131.9, 137.2, 138.7, 144.0, 146.0, 146.4, 147.5, 147.6; HRMS (ESI) m/z calcd. for $C_{34}H_{26}BrO_4$ $[M+H]^+$: 577.1009, found: 577.0999.



(6R,10S)-7-methyl-6-phenyl-10-((E)-styryl)-9-(4-(trifluoromethyl)phenyl)-6H, 10H- [1, 3] dioxolo [4',5':4,5] benzo[1,2-b] furo[3,4-e] oxepine (3fa)

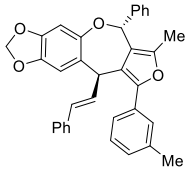
According to general procedure 1: White solid, m.p. = 96-98 ℃; 42 mg, 74% yield; 94% ee; $[\alpha]_D^{20.0}$ = -13.1 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm ×25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =9.7 min, t (minor)

=6.7 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.84 (s, 3H), 4.65 (d, J = 5.8 Hz, 1H), 5.68 (s, 1H), 5.79 (s, 2H), 6.34 (s, 1H), 6.49 (d, J = 15.8 Hz, 1H), 6.65 (s, 1H), 6.81 (dd, J = 6.0, 15.9 Hz, 1H), 7.09 (d, J = 6.4 Hz, 2H), 7.19 (t, J = 7.2 Hz, 1H), 7.24 -7.31 (m, 5H), 7.38 (d, J = 7.5 Hz, 2H), 7.69 (d, J = 8.3 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 44.9, 78.6, 101.3, 107.2, 108.2, 120.5, 122.4, 125.8 (q, J = 3.7 Hz), 126.1, 126.6, 127.4, 128.3, 128.6, 125.7 (q, J = 10.5 Hz), 128.8, 125.8 (q, J = 323.8 Hz), 129.5, 129.8, 129.9, 131.6, 134.5, 137.2, 138.6, 144.1, 145.6, 146.5, 147.6, 148.4; HRMS (ESI) m/z calcd. for $C_{35}H_{26}F_3O_4$ $[M+H]^+$: 567.1777, found: 567.1772.



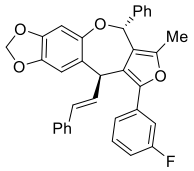
(6R,10S)-7-methyl-9-(4-nitrophenyl)-6-phenyl-10-((E)-styryl)-6H,10H-[1,3] dioxolo [4',5':4,5] benzo[1,2-b] furo[3,4-e] oxepine (3ga)

According to general procedure 1: Red solid, m.p. = 170-172 ℃; 38 mg, 70% yield; 94% ee; $[\alpha]_D^{20.0}$ = -8.1 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm ×25 cm), *n*-hexane/2-propanol = 95/5, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =17.5 min, t (minor) =10.9 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.86 (s, 3H), 4.67 (d, J = 5.9 Hz, 1H), 5.68 (s, 1H), 5.80 (s, 2H), 6.34 (s, 1H), 6.50 (d, J = 16.3 Hz, 1H), 6.66 (s, 1H), 6.80 (dd, J = 5.9, 15.9 Hz, 1H), 7.07 (d, J = 6.4 Hz, 2H), 7.20 (t, J = 7.3 Hz, 1H), 7.24-7.31 (m, 5H), 7.39 (d, J = 7.5 Hz, 2H), 7.80 (d, J = 8.9 Hz, 2H), 8.30 (d, J = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.0, 45.1, 78.5, 101.3, 107.2, 108.2, 121.2, 124.3, 124.4, 126.0, 126.6, 127.6, 128.3, 128.6, 128.9, 129.4, 129.5, 130.1, 131.1, 137.0, 137.1, 138.3, 144.2, 144.9, 146.2, 146.6, 147.6, 149.6; HRMS (ESI) m/z calcd. for $C_{34}H_{26}NO_6$ $[M+H]^+$: 544.1755, found: 544.1728.



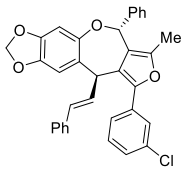
(6R,10S)-6,9-diphenyl-10-((E)-styryl)-7-(m-tolyl)-6H,10H- [1,3] dioxolo [4',5':4,5] benzo[1,2-b] furo[3,4-e] oxepine (3ha)

According to general procedure 1: White solid, m.p. = 88-90℃; 39 mg, 76% yield; 90% ee; $[\alpha]_D^{20.0}$ = -8.8 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm×25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =7.6 min, t (minor) =6.9 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.80 (s, 3H), 2.41 (s, 3H), 4.65 (d, *J* = 6.0 Hz, 1H), 5.68 (s, 1H), 5.76 (s, 2H), 6.34 (s, 1H), 6.50 (d, *J* = 15.9 Hz, 1H), 6.65 (s, 1H), 6.85 (dd, *J* = 6.2, 15.9 Hz, 1H), 7.09 (d, *J* = 6.1 Hz, 2H), 7.16 (dd, *J* =7.6, 15.8 Hz, 2H), 7.22-7.31 (m, 5H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 2H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.50 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 21.7, 45.0, 78.7, 101.2, 107.1, 108.2, 119.9, 120.4, 123.5, 126.5, 127.1, 127.2, 128.2, 128.4, 128.4, 128.5, 128.6, 129.5, 129.6, 130.3, 131.2, 132.3, 137.5, 138.3, 138.9, 144.0, 146.3, 147.0, 147.1, 147.2, 147.6; HRMS (ESI) m/z calcd. for $C_{35}H_{29}O_4$ $[M+H]^+$: 513.2060, found: 513.2056.



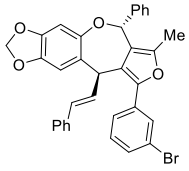
(6R,10S)-9-(3-fluorophenyl)-7-methyl-6-phenyl-10-((E)-styryl)-6H,10H-[1,3] dioxolo[4',5':4,5] benzo[1,2-b]furo[3,4-e]oxepine (3ia)

According to general procedure 1: White solid, m.p. = 84-86 ℃; 35 mg, 68% yield; 93% ee; $[\alpha]_D^{20.0}$ = 1.6 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm ×25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =9.1 min, t (minor) =7.8 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3H), 4.65 (d, *J* = 5.9 Hz, 1H), 5.68 (s, 1H), 5.78 (s, 2H), 6.33 (s, 1H), 6.49 (d, *J* = 15.9 Hz, 1H), 6.66 (s, 1H), 6.80 (dd, *J* = 6.0, 15.9 Hz, 1H), 6.97-7.04 (m, 1H), 7.08 (d, *J* = 6.3 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.23-7.29 (m, 5H), 7.35-7.45 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 44.9, 78.6, 101.2, 107.2, 108.3, 113.0 (d, *J* = 23.1 Hz), 114.1 (d, *J* = 21.2 Hz), 120.3, 121.4, 121.7, 121.8, 126.6, 127.3, 128.2, 128.5, 128.7, 129.5, 129.7, 129.9, 130.3 (d, *J* = 8.5 Hz), 131.8, 133.2 (d, *J* = 8.6 Hz), 137.3, 138.7, 144.0, 145.8 (d, *J* = 2.6 Hz), 146.4, 147.7 (d, *J* = 5.3 Hz), 163.1 (d, *J* = 245.4 Hz); HRMS (ESI) m/z calcd. for $C_{34}H_{26}FO_4$ $[M+H]^+$: 517.1810, found: 517.1807.



(6R,10S)-7-(3-chlorophenyl)-6,9-diphenyl-10-((E)-styryl)-6H,10H-[1,3]dioxolo [4',5':4,5] benzo[1,2-b] furo[3,4-e] oxepine (3ja)

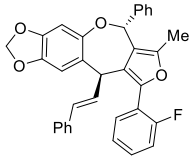
According to general procedure 1: White solid, m.p. = 98-100 ℃; 42 mg, 79% yield; 93% ee; $[\alpha]_D^{20.0}$ = -12.1 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm×25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =8.3 min, t (minor) =7.7 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81 (s, 3H), 4.61 (d, *J* = 6.0 Hz, 1H), 5.67 (s, 1H), 5.78 (s, 2H), 6.34 (s, 1H), 6.51 (d, *J* = 15.9 Hz, 1H), 6.65 (s, 1H), 6.83 (dd, *J* = 6.4, 15.9 Hz, 1H), 7.08 (d, *J* = 6.5 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.23-7.31 (m, 6H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.68 (t, *J* = 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 45.1, 78.6, 101.3, 107.2, 108.2, 120.3, 121.6, 124.2, 126.3, 126.6, 127.2, 127.3, 128.2, 128.5, 128.7, 129.5, 129.8, 129.9, 130.0, 131.8, 132.9, 134.8, 137.3, 138.7, 144.1, 145.6, 146.4, 147.6, 147.8; HRMS (ESI) m/z calcd. for $C_{34}H_{26}ClO_4$ $[M+H]^+$: 533.1514, found: 533.1511.



(6R,10S)-9-(3-bromophenyl)-7-methyl-6-phenyl-10-((E)-styryl)-6H,10H- [1,3] dioxolo [4',5':4,5] benzo[1,2-b] furo[3,4-e] oxepine (3ka)

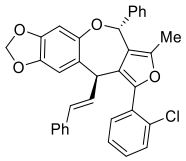
According to general procedure 1: Yellow solid, m.p. = 84-86 ℃; 36 mg, 62% yield; 93% ee; $[\alpha]_D^{20.0}$ = -3.5 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm ×25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =8.5 min, t (minor) =8.1 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3H), 4.59 (d, *J* = 6.4 Hz, 1H), 5.67 (s, 1H), 5.79 (s, 2H), 6.34 (s, 1H), 6.52 (d, *J* = 15.9 Hz, 1H), 6.65 (s, 1H), 6.84 (dd, *J* = 6.5, 15.9 Hz, 1H), 7.08 (d, *J* = 6.5 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.23-7.33 (m, 6H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 45.1, 78.7, 101.3, 107.2, 108.2, 120.2, 121.7, 122.9,

124.6, 126.6, 127.3, 128.2, 128.5, 128.8, 129.2, 129.5, 129.9, 130.0, 130.1, 130.3, 131.7, 133.2, 137.3, 138.7, 144.1, 145.4, 146.4, 147.5, 147.8; HRMS (ESI) m/z calcd. for $C_{34}H_{26}BrO_4$ $[M+H]^+$: 577.1009, found: 577.1014.



(6R,10S)-9-(2-fluorophenyl)-7-methyl-6-phenyl-10-((E)-styryl)-6H,10H-[1,3] dioxolo [4',5':4,5] benzo[1,2-b]furo[3,4-e]oxepine (3la)

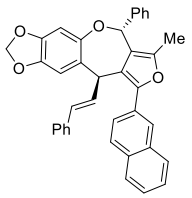
According to general procedure 1: White solid, m.p. = 80-82 ℃; 34 mg, 65% yield; 92% ee; $[\alpha]_D^{20.0}$ = -5.8 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm×25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =11.3 min, t (minor) =7.8 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.79 (s, 3H), 4.51 (d, *J* = 6.3 Hz, 1H), 5.74 (s, 1H), 5.80 (s, 2H), 6.30 (s, 1H), 6.32 (d, *J* = 15.8 Hz, 1H), 6.67 (s, 1H), 6.79 (dd, *J* = 6.4, 15.8 Hz, 1H), 7.09 -7.21 (m, 4H), 7.21-7.26 (m, 2H), 7.26-7.30 (m, 3H), 7.30-7.39 (m, 4H), 7.54 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 44.4, 78.5, 101.2, 107.0, 108.2, 116.3 (d, *J* = 22.0 Hz), 119.2 (d, *J* = 14.3 Hz), 119.4, 123.1, 124.3 (d, *J* = 3.0 Hz), 126.5, 127.1, 128.2, 128.4, 128.7, 129.3, 129.4, 129.9 (d, *J* = 8.3 Hz), 130.0, 130.8 (d, *J* = 3.0 Hz), 132.5, 137.5, 138.9, 141.7, 143.9, 146.3, 147.7, 148.2, 159.6 (d, *J* = 249.7 Hz); HRMS (ESI) m/z calcd. for $C_{34}H_{26}FO_4$ $[M+H]^+$: 517.1810, found: 517.1808.



(6R,10S)-9-(2-chlorophenyl)-7-methyl-6-phenyl-10-((E)-styryl)-6H,10H-[1,3] dioxolo [4',5':4,5] benzo[1,2-b] furo[3,4-e] oxepine (3ma)

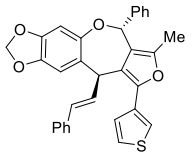
According to general procedure 1: White solid, m.p. = 106-108 ℃; 28 mg, 52% yield; 90% ee; $[\alpha]_D^{20.0}$ = -6.7 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm ×25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =13.3 min, t (minor) =7.8 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3H), 4.41 (d, *J* = 6.9 Hz, 1H), 5.75-5.84 (m, 3H), 6.22 (d, *J* = 15.8 Hz, 1H), 6.34 (s, 1H), 6.66 (s, 1H), 6.70 (dd, *J* = 6.9,

15.8 Hz, 1H), 7.15 (t, *J* = 6.0 Hz, 3H), 7.19-7.31 (m, 7H), 7.32-7.39 (m, 2H), 7.45-7.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.7, 44.4, 78.6, 101.2, 107.0, 108.2, 118.9, 122.7, 126.4, 126.7, 127.1, 128.3, 128.4, 128.7, 129.2, 129.3, 129.9, 130.1, 130.2, 130.3, 132.3, 132.4, 134.7, 137.5, 139.0, 143.9, 144.3, 146.3, 147.4, 147.9; HRMS (ESI) m/z calcd. for $C_{34}H_{26}ClO_4$ $[M+H]^+$: 533.1514, found: 533.1504.



(6R,10S)-7-methyl-9-(naphthalen-2-yl)-6-phenyl-10-((E)-styryl)-6H,10H- [1,3] dioxolo[4',5':4,5] benzo[1,2-b]furo[3,4-e]oxepine (3na)

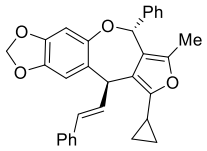
According to general procedure 1: White solid, m.p. = 118-120 ℃; 52 mg, 95% yield; 93% ee; $[\alpha]_D^{20.0}$ = -6.8 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm×25 cm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =6.8 min, t (minor) =5.8 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.85 (s, 3H), 4.75 (d, *J* = 6.1 Hz, 1H), 5.69 (s, 1H), 5.77 (s, 2H), 6.38 (s, 1H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.63 (s, 1H), 6.92 (dd, *J* = 6.3, 16.0 Hz, 1H), 7.12 (d, *J* = 6.0 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.23-7.33 (m, 5H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.46-7.52 (m, 2H), 7.81 (dd, *J* = 1.7 Hz, 8.6, 1H), 7.83-7.88 (m, 2H), 7.91 (d, *J* = 8.6 Hz, 1H), 8.11 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 45.2, 78.8, 101.2, 107.2, 108.2, 120.1, 121.0, 124.6, 125.1, 126.1, 126.4, 126.5, 126.6, 127.3, 127.8, 128.2, 128.3, 128.4, 128.5, 128.7, 129.5, 129.8, 130.3, 132.3, 132.6, 133.5, 137.5, 138.8, 144.0, 146.3, 147.1, 147.4, 147.6; HRMS (ESI) m/z calcd. for $C_{38}H_{29}O_4$ $[M+H]^+$: 549.2060, found: 549.2051.



(6R,10S)-7-methyl-6-phenyl-10-((E)-styryl)-9-(thiophen-3-yl)-6H,10H-[1,3] dioxolo [4',5':4,5] benzo[1,2-b] furo[3,4-e] oxepine (3oa)

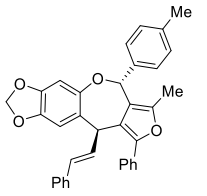
According to general procedure 1: White solid, m.p. = 110-112 ℃; 46 mg, 91% yield; 90% ee; $[\alpha]_D^{20.0}$ = -20.6 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm×25 cm), *n*-

hexane/2-propanol = 97/3, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =14.5 min, t (minor) =9.1 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3H), 4.66 (d, *J* = 6.0 Hz, 1H), 5.68 (s, 1H), 5.78 (s, 2H), 6.33 (s, 1H), 6.46 (d, *J* = 15.9 Hz, 1H), 6.67 (s, 1H), 6.77 (dd, *J* = 6.1, 15.9 Hz, 1H), 7.08 (d, *J* = 6.2 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.22-7.29 (m, 5H), 7.34-7.41 (m, 3H), 7.43 (d, *J* = 5.0, 1H), 7.47 (d, *J* = 3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.7, 44.9, 78.6, 100.0, 101.2, 107.2, 108.3, 119.7, 119.8, 120.2, 126.0, 126.1, 126.5, 127.2, 128.2, 128.5, 128.7, 129.4, 129.5, 130.0, 132.0, 132.2, 137.3, 138.8, 143.9, 144.0, 146.3, 147.7; HRMS (ESI) m/z calcd. for $C_{32}H_{25}O_4S$ $[M+H]^+$: 505.1468, found: 505.1466.



(6R,10S)-9-cyclopropyl-7-methyl-6-phenyl-10-((E)-styryl)-6H,10H- [1,3] dioxolo [4',5':4,5] benzo[1,2-b] furo[3,4-e] oxepine (3pa)

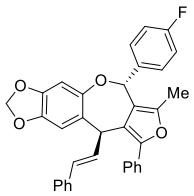
According to general procedure 1: White solid, m.p. = 82-84 ℃; 34 mg, 73% yield; 86% ee; $[\alpha]_D^{20.0}$ = 12.1 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm× 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =12.3 min, t (minor) =7.8 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84-0.94 (m, 4H), 1.68 (s, 3H), 1.88-1.97 (m, 1H), 4.54 (d, *J* = 7.2 Hz, 1H), 5.73 (s, 1H), 5.79 (s, 1H), 5.80 (s, 1H), 6.24 (s, 1H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.73 (s, 1H), 6.77 (*J* = 6.3, 15.9 Hz, 1H), 7.08 (d, *J* = 6.0 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.20-7.28 (m, 5H), 7.35 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.0, 6.1, 7.2, 12.5, 44.7, 78.7, 101.2, 107.2, 108.2, 118.5, 119.3, 126.4, 127.1, 128.1, 128.4, 128.5, 128.6, 129.4, 130.2, 132.6, 137.6, 139.1, 143.9, 144.1, 146.2, 147.9, 148.4; HRMS (ESI) m/z calcd. for $C_{31}H_{27}O_4$ $[M+H]^+$: 463.1904, found: 463.1901.



(6R,10S)-7-methyl-9-phenyl-10-((E)-styryl)-6-(p-tolyl)-6H,10H [1,3] dioxolo

[4',5':4,5] benzo [1,2-b] furo[3,4-e] oxepine (3qa)

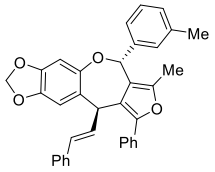
According to general procedure 1: White solid, m.p. = 90-92 ℃; 40 mg, 78% yield; 90% ee; $[\alpha]_D^{20.0}$ = -12.2 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =9.6 min, t (minor) =8.0 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.80 (s, 3H), 2.32 (s, 3H), 4.66 (d, *J* = 5.7 Hz, 1H), 5.71 (s, 1H), 5.77 (s, 1H), 5.78 (s, 1H), 6.30 (s, 1H), 6.48 (d, *J* = 15.9 Hz, 1H), 6.64 (s, 1H), 6.82 (d, *J* = 5.7 Hz, 15.9 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.22-7.28 (m, 2H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 21.3, 44.8, 78.5, 101.2, 107.3, 108.2, 120.1, 120.4, 126.3, 126.5, 127.2, 127.3, 128.5, 128.7, 128.9, 129.4, 129.5, 130.3, 131.3, 132.2, 135.9, 137.5, 138.3, 143.9, 146.3, 146.9, 147.1, 147.7; HRMS (ESI) m/z calcd. for $C_{35}H_{29}O_4$ $[M+H]^+$: 513.2060, found: 513.2055.



(6R,10S)-6-(4-fluorophenyl)-7-methyl-9-phenyl-10-((E)-styryl)-6H,10H- [1,3] dioxolo [4',5':4,5] benzo[1,2-b] furo[3,4-e] oxepine (3ra)

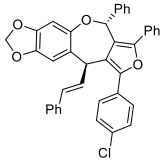
According to general procedure 1: White solid, m.p. = 80-82 ℃; 49 mg, 95% yield; 90% ee; $[\alpha]_D^{20.0}$ = -12.2 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =12.7 min, t (minor) =9.0 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3H), 4.66 (d, *J* = 5.8 Hz, 1H), 5.68 (s, 1H), 5.79 (s, 2H), 6.32 (s, 1H), 6.48 (d, *J* = 15.9 Hz, 1H), 6.65 (s, 1H), 6.80 (dd, *J* = 5.9, 15.9 Hz, 1H), 6.95 (t, *J* = 8.5 Hz, 2H), 7.07 (t, *J* = 6.5 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.22-7.29 (m, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 44.7, 77.9, 101.3, 107.1, 108.3, 115.1 (d, *J* = 21.4 Hz), 119.9, 120.2, 126.3, 126.5, 127.3 (d, *J* = 13.3 Hz), 128.5, 128.8, 129.6, 130.3, 131.1, 131.2, 131.3, 132.1, 135.0 (d, *J* = 3.2 Hz),

137.4, 144.1, 146.4, 147.0, 147.1, 147.4, 162.8 (d, *J* = 247.7 Hz); HRMS (ESI) m/z calcd. for $C_{34}H_{26}FO_4$ $[M+H]^+$: 517.1810, found: 517.1806.



(6R,10S)-7-methyl-9-phenyl-10-((E)-styryl)-6-(m-tolyl)-6H,10H-[1,3]dioxolo [4',5':4,5] benzo[1,2-b] furo[3,4-e] oxepine (3sa)

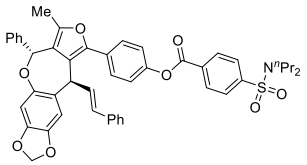
According to general procedure 1: White solid, m.p. = 92-94 ℃; 30 mg, 59% yield; 90% ee; $[\alpha]_D^{20.0}$ = -18.9 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm×25 cm), *n*-hexane/2-propanol = 95/5, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =7.1 min, t (minor) =5.9 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3H), 2.29 (s, 3H), 4.67 (d, *J* = 5.9 Hz, 1H), 5.70 (s, 1H), 5.78 (s, 2H), 6.29 (s, 1H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.65 (s, 1H), 6.86-6.79 (m, 2H), 6.96 (s, 1H), 7.07-7.22 (m, 3H), 7.26 (t, *J* = 8.3 Hz, 2H) 7.31 (t, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 21.5, 44.8, 78.8, 101.2, 107.2, 108.3, 120.0, 120.4, 126.3, 126.5, 126.6, 127.2, 127.3, 128.0, 128.5, 128.8, 129.4, 129.5, 130.1, 130.2, 131.3, 132.3, 137.5, 137.7, 138.8, 143.9, 146.3, 146.9, 147.2, 147.8; HRMS (ESI) m/z calcd. for $C_{35}H_{29}O_4$ $[M+H]^+$: 513.2060, found: 513.2056.



(6R,10S)-9-(4-chlorophenyl)-6,7-diphenyl-10-((E)-styryl)-6H,10H- [1,3] dioxolo [4',5':4,5] benzo[1,2-b] furo[3,4-e] oxepine (3ta)

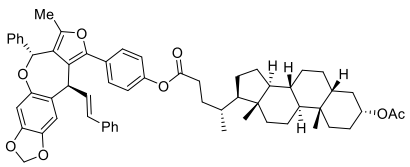
According to general procedure 1: White solid, m.p. = 230-232 ℃; 45 mg, 75% yield; 93% ee; $[\alpha]_D^{20.0}$ = -25.8 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm×25 cm), *n*-hexane/2-propanol = 95/5, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =10.5 min, t (minor) =7.7 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.69 (d, *J* = 5.9 Hz, 1H), 5.69 (s, 1H), 5.75 (s, 1H), 5.76 (s, 1H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.66 (s, 1H), 6.71 (s, 1H), 6.78 (dd, *J* = 6.0, 15.9 Hz, 1H), 7.09-7.22 (m, 9H), 7.22 -7.29 (m, 2H), 7.37 (dd, *J* = 2.4, 8.2 Hz, 4H),

7.46 (d, J = 8.5 Hz, 2H), 7.73 (d, J = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.9, 79.3, 101.2, 107.1, 107.9, 122.0, 122.2, 125.5, 126.6, 127.3, 127.4, 128.0, 128.3, 128.4, 128.5, 128.7, 129.1, 129.4, 129.5, 129.6, 129.7, 130.4, 132.1, 133.7, 137.2, 138.5, 144.1, 146.5, 147.2, 147.4, 148.2; HRMS (ESI) m/z calcd. for $C_{39}H_{28}ClO_4$ $[M+H]^+$: 595.1671, found: 595.1666.



4-((6R,10S)-7-methyl-6-phenyl-10-((E)-styryl)-6H,10H-[1,3]dioxolo[4',5':4,5] benzo[1,2-b]furo[3,4-e]oxepin-9-yl)phenyl4-(N,N-dipropylsulfamoyl)benzoate (3ua)

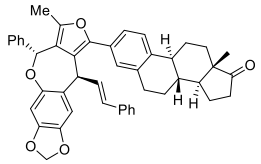
According to general procedure 1: White solid, m.p. = 108-110 ℃; 61 mg, 78% yield; 94% ee; $[\alpha]_D^{20.0}$ = 11.8 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm ×25 cm), *n*-hexane/2-propanol = 80/20, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =16.6 min, t (minor) =13.1 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J = 7.4 Hz, 6H), 1.56-1.61 (m, 4H), 1.83 (s, 3H), 3.14 (t, J = 7.4 Hz, 4H), 4.65 (d, J = 5.9 Hz, 1H), 5.68 (s, 1H), 5.80 (s, 2H), 6.35 (s, 1H), 6.50 (d, J = 15.9 Hz, 1H), 6.68 (s, 1H), 6.82 (dd, J = 5.9, 15.9 Hz, 1H), 7.10 (d, J = 6.8 Hz, 2H), 7.18 (t, J = 7.3 Hz, 1H), 7.25-7.33 (m, 7H), 7.39 (d, J = 7.7 Hz, 2H), 7.73 (d, J = 8.3 Hz, 2H), 7.96 (d, J = 8.1 Hz, 2H), 8.35 (d, J = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.3, 12.9, 22.0, 44.8, 50.0, 78.7, 101.2, 107.2, 108.2, 120.1, 120.7, 121.9, 126.5, 127.2, 127.3, 127.5, 128.2, 128.5, 128.7, 129.5, 129.6, 130.0, 130.9, 132.0, 132.2, 132.8, 137.3, 138.7, 144.0, 145.1, 146.2, 146.4, 147.4, 147.6, 149.7, 164.0; HRMS (ESI) m/z calcd. for $C_{47}H_{44}NO_8S$ $[M+H]^+$: 782.2782, found: 782.2789.



4-((6R,10S)-7-methyl-6-phenyl-10-((E)-styryl)-6H,10H [1,3] dioxolo[4',5':4,5] benzo[1,2-b] furo [3,4-e] oxepin-9-yl) phenyl-(R)-4-((3R,5R,8R,9S,10S,13R,14S, 17R)-3-acetoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-

yl) pentanoate (3va)

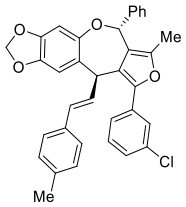
According to general procedure 1: White solid, m.p. = 122-124 ℃; 60 mg, 66% yield; 93% ee; $[\alpha]_D^{20.0}$ = 14.3 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm×25 cm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =14.5 min, t (minor) =9.2 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.68 (s, 3H), 0.93 (s, 3H), 1.00 (d, J = 6.1 Hz, 3H), 1.05-1.20 (m, 5H), 1.21-1.36 (m, 5H), 1.34-1.52 (m, 8H), 1.69 (d, J = 10.1 Hz, 2H), 1.81 (s, 3H), 1.82-2.01 (m, 6H), 2.03 (s, 3H), 2.46-2.55 (m, 1H), 2.59-2.68 (m, 1H), 4.62 (d, J = 6.0 Hz, 1H), 4.71-4.73 (m, 1H), 5.67 (s, 1H), 5.79 (s, 2H), 6.33 (s, 1H), 6.48 (d, J = 15.8 Hz, 1H), 6.66 (s, 1H), 6.81 (dd, J = 6.8, 15.9 Hz, 1H), 7.09 (d, J = 6.8 Hz, 2H), 7.14-7.21 (m, 3H), 7.23-7.30 (m, 5H), 7.38 (d, J = 7.6 Hz, 2H), 7.65 (d, J = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.2, 12.8, 18.4, 20.9, 21.6, 23.4, 24.3, 26.4, 26.7, 27.1, 28.4, 31.1, 31.6, 32.4, 34.7, 35.1, 35.5, 35.9, 40.3, 40.5, 42.0, 42.9, 44.8, 56.1, 56.6, 74.5, 78.7, 101.2, 107.2, 108.2, 120.0, 120.4, 121.9, 126.5, 127.3, 127.4, 128.2, 128.5, 128.7, 128.9, 129.5, 129.6, 130.1, 132.1, 137.3, 138.8, 144.0, 146.3, 146.4, 147.2, 147.6, 149.9, 170.7, 172.8; HRMS (ESI) m/z calcd. for $C_{60}H_{67}O_8$ $[M+H]^+$: 915.4831, found: 915.4827.



(8R,9S,13S,14S)-13-methyl-1-((6R,10S)-7-methyl-6-phenyl-10-((E)-styryl)-6H,10H-[1,3] dioxolo[4',5':4,5]benzo[1,2-b]furo[3,4-e]oxepin-9-yl)-6,7,8, 9,11,12,13,14,15,16-dwecahydro-17H-cyclopenta[a]phenanthren-17-one (3wa)

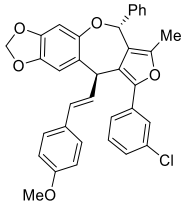
According to general procedure 1: White solid, m.p. = 258-260 ℃; 55 mg, 82% yield; 89% ee; $[\alpha]_D^{20.0}$ = 54.3 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm×25 cm), *n*-hexane/2-propanol = 95/5, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =12.1 min, t (minor) =10.5 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (s, 3H), 1.44-1.59 (m, 4H), 1.61-1.69 (m, 2H), 1.80 (s, 3H), 1.97-2.11 (m, 3H), 2.17 (t, J = 8.9 Hz, 1H), 2.31-2.40 (m, 1H), 2..42-2.56 (m, 2H), 2.88-3.10 (m, 2H), 4.65 (d, J = 6.0 Hz, 1H), 5.68 (s, 1H), 5.77 (s, 2H), 6.34 (s, 1H), 6.50 (d, J = 15.9 Hz, 1H), 6.64 (s, 1H), 6.85 (dd, J = 6.3, 15.9 Hz,

1H), 7.09 (d, *J* = 6.3 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 1H) 7.26 (t, *J* = 7.2 Hz, 5H), 7.37 (t, *J* = 8.7 Hz, 3H), 7.40-7.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 13.9, 21.7, 25.8, 26.6, 29.5, 31.7, 35.9, 38.2, 44.5, 45.0, 48.0, 50.6, 78.7, 101.2, 107.1, 108.2, 119.8, 120.0, 123.8, 125.7, 126.5, 126.9, 127.2, 128.1, 128.5, 128.6, 128.9, 129.4, 129.5, 130.3, 132.4, 136.8, 137.4, 138.9, 139.0, 143.9, 146.2, 146.8, 147.0, 147.6, 220.8; HRMS (ESI) m/z calcd. for $C_{46}H_{43}O_5$ $[M+H]^+$: 675.3105, found: 675.3114.



(6R,10S)-9-(3-chlorophenyl)-7-methyl-10-((E)-4-methylstyryl)-6-phenyl-6H,10H-[1,3] dioxolo[4',5':4,5]benzo[1,2-b]furo[3,4-e]oxepine (3jb)

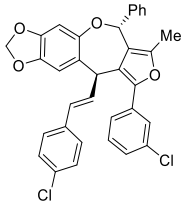
According to general procedure 1: White solid, m.p. = 190-192 ℃; 41 mg, 75% yield; 90% ee; $[\alpha]_D^{20.0}$ = -3.5 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm×25 cm), *n*-hexane/2-propanol = 98/2, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =11.1 min, t (minor) =11.6 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81 (s, 3H), 2.30 (s, 3H), 4.59 (d, *J* = 6.3 Hz, 1H), 5.67 (s, 1H), 5.78 (s, 2H), 6.34 (s, 1H), 6.48 (d, *J* = 15.9 Hz, 1H), 6.65 (s, 1H), 6.77 (dd, *J* = 6.5, 15.9 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 4H), 7.23-7.31 (m, 6H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 21.2, 45.1, 78.6, 101.2, 107.1, 108.2, 120.3, 121.7, 124.2, 126.3, 126.5, 127.2, 128.2, 128.7, 129.2, 129.4, 129.7, 130.0, 130.1, 130.7, 132.9, 134.5, 134.7, 137.1, 138.7, 144.0, 145.5, 146.4, 147.5, 147.7; HRMS (ESI) m/z calcd. for $C_{35}H_{28}ClO_4$ $[M+H]^+$: 547.1671, found: 547.1671.



(6R,10S)-9-(3-chlorophenyl)-10-((E)-4-methoxystyryl)-7-methyl-6-phenyl-6H,10H-[1,3] dioxolo[4',5':4,5]benzo[1,2-b]furo[3,4-e]oxepine (3jc)

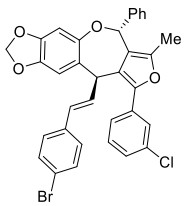
According to general procedure 1: White solid, m.p. = 80-82 ℃; 38 mg, 68% yield;

97% ee; $[\alpha]_D^{20.0}$ = -5.1 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm×25 cm), *n*-hexane/2-propanol = 99/1, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) = 29.6 min, t (minor) =33.3 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81 (s, 3H), 3.78 (s, 3H), 4.59 (d, *J* = 6.3 Hz, 1H), 5.67 (s, 1H), 5.78 (s, 2H), 6.34 (s, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.65 (s, 1H), 6.69 (dd, *J* = 6.4, 15.9 Hz, 1H), 6.81 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 6.2 Hz, 2H), 7.21-7.30 (m, 4H), 7.29-7.39 (m, 3H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 45.1, 55.4, 78.6, 101.2, 107.2, 108.2, 114.0, 120.3, 121.8, 124.2, 126.3, 127.1, 127.7, 128.2, 128.7, 129.3, 129.4, 129.6, 130.0, 130.1, 130.2, 132.9, 134.7, 138.7, 144.0, 145.5, 146.3, 147.5, 147.7, 159.1; HRMS (ESI) m/z calcd. for $C_{35}H_{28}ClO_5$ $[M+H]^+$: 563.1620, found: 563.1620.



(6R,10S)-9-(3-chlorophenyl)-10-((E)-4-chlorostyryl)-7-methyl-6-phenyl-6H,10H-[1,3] dioxolo[4',5':4,5]benzo[1,2-b]furo[3,4-e]oxepine (3jd)

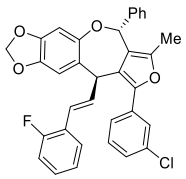
According to general procedure 1: White solid, m.p. = 90-92 ℃; 32 mg, 57% yield; 95% ee; $[\alpha]_D^{20.0}$ = -1.8 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm×25 cm), *n*-hexane/2-propanol = 98/2, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =10.3 min, t (minor) =10.8 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3H), 4.60 (d, *J* = 6.1 Hz, 1H), 5.67 (s, 1H), 5.79 (s, 2H), 6.33 (s, 1H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.65 (s, 1H), 6.80 (dd, *J* = 6.4, 15.9 Hz, 1H), 7.02-7.13 (m, 2H), 7.21-7.34 (m, 8H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 45.0, 78.7, 101.3, 107.2, 108.2, 120.2, 121.4, 124.1, 126.3, 127.3, 127.8, 128.2, 128.6, 128.7, 128.8, 129.5, 129.7, 130.0, 132.5, 132.8, 132.9, 134.7, 135.8, 138.6, 144.1, 145.6, 146.5, 147.5, 147.8; HRMS (ESI) m/z calcd. for $C_{34}H_{25}Cl_2O_4$ $[M+H]^+$: 567.1124, found: 567.1126.



(6R,10S)-10-((E)-4-bromostyryl)-9-(3-chlorophenyl)-7-methyl-6-phenyl-6H,10H-

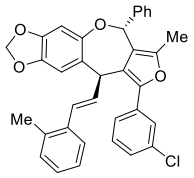
[1,3] dioxolo- [4',5':4,5] benzo[1,2-b] furo[3,4-e] oxepine (3je)

According to general procedure 1: White solid, m.p. = 98-100 ℃; 46 mg, 75% yield; 95% ee; $[\alpha]_D^{20.0}$ = -8.8 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm×25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =10.9 min, t (minor) =11.8 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3H), 4.59 (d, J = 6.3 Hz, 1H), 5.67 (s, 1H), 5.78 (s, 2H), 6.33 (s, 1H), 6.44 (d, J = 15.9 Hz, 1H), 6.64 (s, 1H), 6.81 (dd, J =6.3, 15.9 Hz, 1H), 7.07 (d, J = 7.0 Hz, 2H), 7.22-7.32 (m, 6H), 7.34 -7.41 (m, 3H), 7.50 (d, J = 7.7 Hz, 1H), 7.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 45.0, 78.7, 101.3, 107.2, 108.2, 120.2, 121.0, 121.3, 124.1, 126.3, 127.3, 128.1, 128.2, 128.7, 128.8, 129.5, 129.7, 130.0, 131.6, 132.6, 132.8, 134.7, 136.2, 138.6, 144.1, 145.6, 146.5, 147.5, 147.8; HRMS (ESI) m/z calcd. for $C_{34}H_{25}ClBrO_4$ $[M+H]^+$: 611.0619, found: 611.0617.



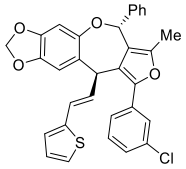
(6R,10S)-9-(3-chlorophenyl)-10-((E)-2-fluorostyryl)-7-methyl-6-phenyl-6H,10H-[1,3] dioxolo [4',5':4,5]benzo[1,2-b]furo[3,4-e]oxepine (3jf)

According to general procedure 1: White solid, m.p. = 154-156 ℃; 42 mg, 76% yield; 84% ee; $[\alpha]_D^{20.0}$ = 11.0 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm ×25 cm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) = 13.6 min, t (minor) =15.4 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81 (s, 3H), 4.63 (d, J = 6.4 Hz, 1H), 5.67 (s, 1H), 5.78 (s, 2H), 6.34 (s, 1H), 6.66 (s, 1H), 6.70 (d, J = 16.1 Hz, 1H), 6.92 (dd, J = 6.4, 16.0 Hz, 1H), 6.96-7.11 (m, 4H), 7.12-7.19 (m, 1H), 7.23-7.30 (m, 4H), 7.37 (t, J = 7.6 Hz, 1H), 7.46-7.54 (m, 2H), 7.67 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 45.4, 78.7, 101.3, 107.2, 108.2, 115.7 (d, J = 22.2 Hz), 120.2, 121.3, 122.2 (d, J = 4.0 Hz), 124.0 (d, J = 3.5 Hz), 124.2, 125.1 (d, J = 12.2 Hz), 126.3, 127.3, 127.5 (d, J = 3.9 Hz), 128.2, 128.6 (d, J = 8.3 Hz), 128.8, 129.5, 129.8, 130.0, 132.8, 134.2 (d, J = 4.4 Hz), 134.8, 138.6, 144.1, 145.7, 146.5, 147.5, 147.8, 160.2 (d, J = 248.8 Hz); HRMS (ESI) m/z calcd. for $C_{34}H_{25}ClFO_4$ $[M+H]^+$: 551.1420, found: 551.1424.



(6R,10S)-9-(3-chlorophenyl)-7-methyl-10-((E)-2-methylstyryl)-6-phenyl-6H,10H-[1,3] dioxolo[4',5':4,5]benzo[1,2-b]furo[3,4-e]oxepine (3jg)

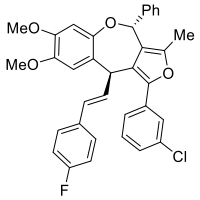
According to general procedure 1: White solid, m.p. = 78-80 ℃; 32 mg, 58% yield; 96% ee; $[\alpha]_D^{20.0}$ = 5.4 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm×25 cm), *n*-hexane/2-propanol = 99/1, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) = 10.4 min, t (minor) =9.4 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81 (s, 3H); 2.32 (s, 3H), 4.63 (d, J = 5.4 Hz, 1H), 5.68 (s, 1H), 5.78 (s, 2H), 6.33 (s, 1H), 6.66 (s, 1H), 6.72 (d, J = 5.3 Hz, 1H), 6.73 (s, 1H), 7.14 -7.05 (m, 5H), 7.20-7.32 (m, 4H), 7.36 (t, J = 7.9 Hz, 1H), 7.43-7.49 (m, 1H), 7.57 (d, J = 7.7 Hz, 1H), 7.70 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 20.0, 45.4, 78.7, 101.2, 107.2, 108.2, 120.2, 121.8, 124.2, 126.0, 126.1, 126.2, 127.2, 127.3, 127.8, 128.2, 128.7, 129.5, 130.0, 130.1, 130.2, 133.0, 133.1, 134.7, 135.4, 136.5, 138.7, 144.1, 145.5, 146.4, 147.5, 147.8; HRMS (ESI) m/z calcd. for $C_{35}H_{28}ClO_4$ $[M+H]^+$: 547.1671, found: 547.1671.



(6R,10S)-9-(3-chlorophenyl)-7-methyl-6-phenyl-10-((E)-2-(thiophen-2-yl)vinyl)-6H,10H-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]furo[3,4-e]oxepine (3jh)

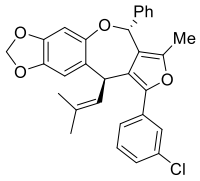
According to general procedure 1: White solid, m.p. = 160-162 ℃; 41 mg, 76% yield; 94% ee; $[\alpha]_D^{20.0}$ = 5.2 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm×25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =9.4 min, t (minor) =8.1 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3H), 4.58 (s, 1H), 5.67 (s, 1H), 5.79 (s, 2H), 6.33 (s, 1H), 6.61 (s, 1H), 6.62 (d, J = 11.6 Hz, 2H), 6.92 (d, J = 4.3 Hz, 2H), 7.04 -7.14 (m, 3H), 7.23-7.33 (m, 4H), 7.37 (t, J = 7.9 Hz, 1H), 7.50 (d, J = 7.8 Hz, 1H), 7.65 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 44.7, 78.6, 101.3, 107.2, 108.2, 120.3, 121.2, 123.1, 123.9, 124.1, 125.5, 126.3, 127.2, 127.3, 128.2, 128.8, 129.4, 129.6, 130.1,

131.4, 132.8, 134.8, 138.6, 142.4, 144.0, 145.6, 146.5, 147.6, 147.8; HRMS (ESI) m/z calcd. for $C_{32}H_{24}ClO_4S$ $[M+H]^+$: 539.1078, found: 539.1077.



(4R,10S)-1-(3-chlorophenyl)-10-((E)-4-fluorostyryl)-7,8-dimethoxy-3-methyl-4-phenyl-4H,10H-benzo[b]furo[3,4-e] oxepine (3ji)

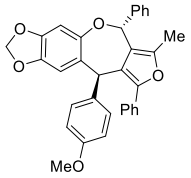
According to general procedure 1: White solid, m.p. = 80-82 ℃; 41 mg, 72% yield; 94% ee; $[\alpha]_D^{20.0}$ = -11.5 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm×25 cm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) = 5.2 min, t (minor) =11.2 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.84 (s, 3H), 3.39 (s, 3H), 3.81 (s, 3H), 4.63 (d, *J* = 6.1 Hz, 1H), 5.66 (s, 1H), 6.36 (s, 1H), 6.49 (d, *J* = 15.9 Hz, 1H), 6.66 (s, 1H), 6.77 (dd, *J* = 6.2, 15.9 Hz, 1H), 6.96 (t, *J* = 8.6 Hz, 2H), 7.05 (d, *J* = 6.0 Hz, 2H), 7.21-7.32 (m, 4H), 7.33-7.43 (m, 3H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.70 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 44.8, 55.8, 56.2, 78.6, 109.7, 111.4, 115.4 (d, *J* = 21.5 Hz), 120.3, 121.8, 124.1, 126.2, 127.2, 128.0 (d, *J* = 7.9 Hz), 128.1, 128.2, 128.6 (d, *J* = 4.5 Hz), 129.4, 130.0, 131.6, 131.7, 133.0, 133.4 (d, *J* = 3.3 Hz), 134.7, 138.9, 145.5, 145.6, 146.6, 147.7, 147.9, 162.2 (d, *J* = 246.4 Hz); HRMS (ESI) m/z calcd. for $C_{35}H_{29}ClFO_4$ $[M+H]^+$: 567.1733, found: 567.1734.



(6R,10S)-9-(3-chlorophenyl)-7-methyl-10-(2-methylprop-1-en-1-yl)-6-phenyl-6H,10H-[1,3] dioxolo[4',5':4,5]benzo[1,2-b]furo[3,4-e]oxepine (3jm)

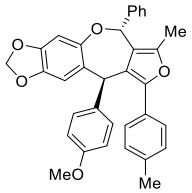
According to general procedure 1: Yellow oil, 25 mg, 52% yield; 73% ee; $[\alpha]_D^{20.0}$ = -18.5 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm×25 cm), *n*-hexane/2-propanol = 98/2, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) =5.9 min, t (minor) =5.0 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.76 (s, 3H), 1.80 (s, 3H), 1.84 (s, 3H), 4.60 (d, *J* = 9.3 Hz, 1H), 5.64 (s, 1H), 5.76 (s, 2H), 6.10 (d, *J* = 9.2 Hz, 1H), 6.35 (s, 1H), 6.59 (s, 1H), 7.07 (d,

J = 7.0 Hz, 2H), 7.22-7.29 (m, 4H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 18.1, 26.0, 40.7, 78.8, 101.1, 107.3, 107.8, 120.1, 123.6, 124.4, 126.5, 126.6, 127.0, 128.2, 128.7, 129.6, 129.9, 131.2, 131.7, 133.1, 134.6, 138.7, 143.8, 145.1, 145.8, 147.0, 147.6; HRMS (ESI) m/z calcd. for $C_{30}H_{26}ClO_4$ $[M+H]^+$: 485.1952, found: 485.1959.



(6R,10S)-10-(4-methoxyphenyl)-7-methyl-6,9-diphenyl-6H,10H- [1,3]-dioxolo [4',5':4,5] benzo[1,2-b] furo[3,4-e] oxepine (3aj)

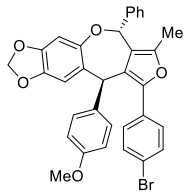
According to general procedure 2: White solid, m.p. = 158-160 ℃; 38 mg, 76% yield; 92% ee; $[\alpha]_D^{20.0}$ = -78.3 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm×25 cm), *n*-hexane/2-propanol = 95/5, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) = 10.6 min, t (minor) =7.1 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 1.82 (s, 3H), 3.77 (s, 3H), 5.12 (s, 1H), 5.59 (s, 1H), 5.79 (s, 1H), 5.80 (s, 1H), 6.25 (s, 1H), 6.78 (s, 1H), 6.83 (d, *J* = 8.6 Hz, 2H), 7.07 (d, *J* = 5.6 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.23 -7.31 (m, 4H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 13.0, 45.1, 55.2, 78.7, 101.2, 107.6, 109.0, 113.7, 120.0, 120.5, 126.0, 127.2, 128.1, 128.2, 128.6, 128.8, 129.5, 131.2, 131.9, 135.9, 138.8, 143.8, 146.2, 147.0, 147.3, 147.4, 157.9; HRMS (ESI) m/z calcd. for $C_{33}H_{27}O_5$ $[M+H]^+$: 503.1853, found: 503.1852.



(6R,10S)-10-(4-methoxyphenyl)-7-methyl-6-phenyl-9-(p-tolyl)-6H,10H-[1,3] dioxolo[4',5':4,5]benzo[1,2-b]furo[3,4-e]oxepine (3bj)

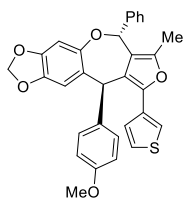
According to general procedure 2: White solid, m.p. = 200-202 ℃; 30 mg, 58% yield; 88% ee; $[\alpha]_D^{20.0}$ = -188.7 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm × 25 cm), *n*-

hexane/2-propanol = 95/5, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) = 10.8 min, t (minor) = 6.8 min]**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.80 (s, 3H), 2.36 (s, 3H), 3.77 (s, 3H), 5.09 (s, 1H), 5.58 (s, 1H), 5.80 (s, 1H), 5.81 (s, 1H), 6.24 (s, 1H), 6.77 (s, 1H), 6.83 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 4.0 Hz, 2H), 7.18 (dd, *J* = 4.2, 8.3 Hz, 4H), 7.20-7.26 (m, 2H), 7.26-7.31 (m, 1H), 7.38 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.0, 21.3, 45.1, 55.2, 78.7, 101.2, 107.6, 109.0, 113.7, 119.8, 119.9, 126.0, 128.1, 128.2, 128.4, 128.6, 129.4, 129.5, 132.0, 136.0, 137.1, 138.9, 143.7, 146.2, 147.0, 147.1, 147.4, 157.9; HRMS (ESI) m/z calcd. for $C_{34}H_{27}O_5$ $[M-H]^+$: 515.1853, found: 515.1850.



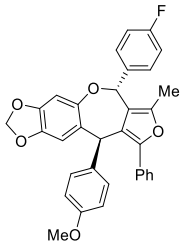
(6R,10S)-9-(4-bromophenyl)-10-(4-methoxyphenyl)-7-methyl-6-phenyl-6H,10H-[1,3] dioxolo[4',5':4,5]benzo[1,2-b]furo[3,4-e]oxepine (3ej)

According to general procedure 2: White solid, m.p. = 104-106 ℃; 36 mg, 62% yield; 90% ee; $[\alpha]_D^{20.0}$ = -58.2 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 95/5, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) = 12.1 min, t (minor) = 7.5 min]**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81 (s, 3H), 3.78 (s, 3H), 5.04 (s, 1H), 5.58 (s, 1H), 5.81 (s, 2H), 6.25 (s, 1H), 6.77 (s, 1H), 6.83 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 7.1 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.22-7.26 (m, 2H), 7.26 -7.29 (m, 1H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.0, 45.3, 55.3, 78.6, 101.2, 107.7, 108.9, 113.8, 120.3, 121.2, 126.3, 127.4, 128.2, 128.7, 129.5, 130.0, 131.4, 131.7, 131.9, 135.5, 138.6, 143.8, 146.2, 146.3, 147.0, 147.8, 158.0; HRMS (ESI) m/z calcd. for $C_{33}H_{26}BrO_5$ $[M+H]^+$: 581.0958, found: 581.0962.



(6R,10S)-10-(4-methoxyphenyl)-7-methyl-6-phenyl-9-(thiophen-3-yl)-6H,10H-[1,3] dioxolo[4',5':4,5]benzo[1,2-b]furo[3,4-e]oxepine (3oj)

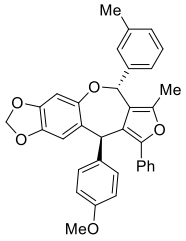
According to general procedure 2: White solid, m.p. =150-152 ℃; 31 mg, 62% yield; 90% ee; $[\alpha]_D^{20.0}$ = -123.1 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm×25 cm), *n*-hexane/2-propanol = 95/5, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) = 13.7 min, t (minor) =7.8min]**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3H), 3.75 (s, 3H), 5.10 (s, 1H), 5.60 (s, 1H), 5.79 (s, 1H), 5.80 (s, 1H), 6.25 (s, 1H), 6.80 (s, 2H), 6.83 (s, 1H),7.06 (d, *J* = 7.2 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.21-7.28 (m, 4H), 7.30 (d, *J* = 5.1 Hz, 1H), 7.34 (dd, *J* = 2.9, 5.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 45.2, 55.3, 78.6, 101.2, 107.7, 109.0, 113.8, 119.8, 119.9, 125.8, 126.1, 128.1, 128.2, 128.3, 128.7, 129.5, 131.5, 132.1, 135.6, 138.7, 143.8, 144.5, 146.3, 146.6, 147.1, 158.0; HRMS (ESI) m/z calcd. for $C_{31}H_{25}O_5S$ $[M+H]^+$: 509.1417, found: 509.1421.



(6R,10S)-6-(4-fluorophenyl)-10-(4-methoxyphenyl)-7-methyl-9-phenyl-6H,10H-[1,3] dioxolo[4',5':4,5] benzo[1,2-b]furo[3,4-e]oxepine (3rj)

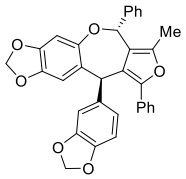
According to general procedure 2: White solid, m.p. = 168-170 ℃; 37 mg, 72% yield; 89% ee; $[\alpha]_D^{20.0}$ = -59.6 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 95/5, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) = 14.7 min, t (minor) =8.2 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.83 (s, 3H), 3.77 (s, 3H), 5.11 (s, 1H), 5.59 (s, 1H), 5.82 (s, 1H), 5.83 (s, 1H), 6.24 (s, 1H), 6.78 (s, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.94 (t, *J* = 8.5 Hz, 2H), 7.05 (s, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.0, 45.1, 55.3, 77.8, 101.3, 107.6, 109.1, 113.7, 115.1 (d, *J* = 21.4 Hz), 119.9, 120.3, 126.0, 127.3, 128.2, 128.8, 131.1, 131.3 (d, *J* = 8.4 Hz), 132.1, 134.9 (d, *J* = 3.2 Hz), 135.8,

143.9, 146.3, 146.7, 147.3, 147.4, 158.0, 162.8 (d, J = 247.3 Hz); HRMS (ESI) m/z calcd. for $C_{33}H_{26}FO_5$ $[M+H]^+$: 521.1759, found: 521.1757.



(6R,10S)-10-(4-methoxyphenyl)-7-methyl-9-phenyl-6-(m-tolyl)-6H,10H-[1,3] dioxolo [4',5':4,5]benzo[1,2-b] furo [3,4-e] oxepine (3sj)

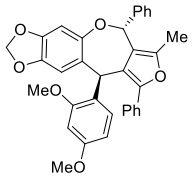
According to general procedure 2: White solid, m.p. =86-87 ℃; 37 mg, 72% yield; 84% ee; $[\alpha]_D^{20.0}$ = -51.9 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 95/5, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) = 9.7 min, t (minor) = 6.7 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3H), 2.28 (s, 3H), 3.77 (s, 3H), 5.12 (s, 1H), 5.61 (s, 1H), 5.79 (s, 1H), 5.81 (s, 1H), 6.20 (s, 1H), 6.78 (s, 1H), 6.83 (d, J = 8.6 Hz, 2H), 6.92 (s, 1H), 7.09 (t, J = 7.6 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 7.23-7.31 (m, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.50 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.1 21.5, 45.1, 55.3, 78.7, 101.2, 107.7, 109.0, 113.7, 120.1, 120.5, 126.0, 126.6, 127.2, 127.9, 128.2, 128.8, 129.4, 130.2, 131.2, 131.9, 135.9, 137.7, 138.7, 143.7, 146.2, 147.1, 147.2, 147.4, 157.9; HRMS (ESI) m/z calcd. for $C_{34}H_{29}O_5$ $[M+H]^+$: 517.2010, found: 517.2007.



(6R,10S)-10-(benzo[d][1,3] dioxol-5-yl)-7-methyl-6,9-diphenyl-6H,10H-[1,3] Dioxolo [4',5':4,5] benzo[1,2-b] furo[3,4-e] oxepine (3ak)

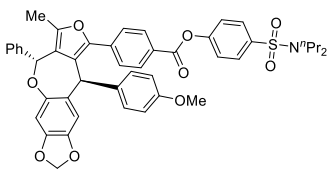
According to general procedure 2: White solid, m.p. = 82-84 ℃; 31 mg, 61% yield; 90% ee; $[\alpha]_D^{20.0}$ = -95.1 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm × 25 cm), *n*-

hexane/2-propanol = 95/5, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) = 8.8 min, t (minor) = 7.3 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81 (s, 3H), 5.07 (s, 1H), 5.59 (s, 1H), 5.81 (s, 2H), 5.91 (s, 1H), 5.93 (s, 1H), 6.25 (s, 1H), 6.73-6.80 (m, 4H), 7.08 (s, 2H), 7.22-7.32 (m, 4H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.0, 45.5, 78.7, 101.0, 101.2, 107.7, 108.0, 108.1, 109.0, 119.9, 120.2, 120.3, 126.0, 127.3, 128.2, 128.7, 128.8, 129.5, 131.1, 131.8, 137.9, 138.7, 143.8, 145.9, 146.3, 147.0, 147.4, 147.5, 147.7; HRMS (ESI) m/z calcd. for $C_{33}H_{25}O_6$ $[M+H]^+$: 517.1646, found: 517.1651.



(6R,10S)-10-(2,4-dimethoxyphenyl)-7-methyl-6,9-diphenyl-6H,10H-[1,3]dioxolo [4',5':4,5] benzo[1,2-b]furo[3,4-e]oxepine (3al)

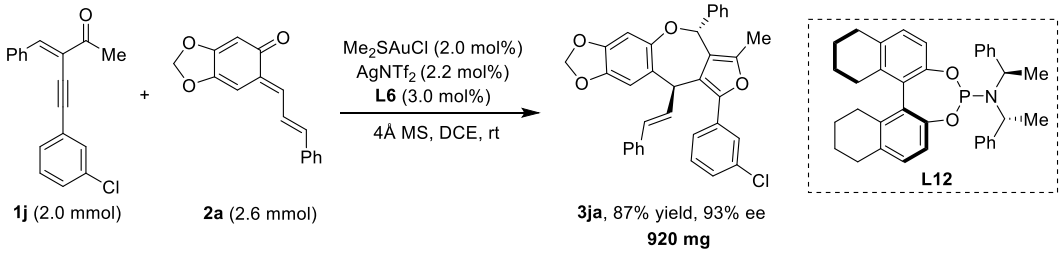
According to general procedure 2: White solid, m.p. = 82-84 ℃; 37 mg, 70% yield; 80% ee; $[\alpha]_D^{20.0}$ = -73.2 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 95/5, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) = 6.5 min, t (minor) =16.6 min]**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88 (s, 3H), 3.78 (s, 3H), 3.83 (s, 3H), 5.43 (s, 1H), 5.51 (s, 1H), 5.74 (s, 2H), 6.45-6.51 (m, 3H), 6.86 (s, 1H), 7.10 (d, *J* = 5.2 Hz, 2H), 7.21-7.28 (m, 4H), 7.30-7.39 (m, 4H),7.55 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 39.9, 55.4, 55.5, 78.7, 98.7, 100.9, 104.0, 106.9, 110.0, 121.0, 121.3, 124.8, 125.9, 126.9, 128.1, 128.5, 128.6, 129.7, 130.8, 131.2, 138.8, 139.5, 143.3, 145.6, 146.6, 146.7, 147.3, 157.3, 159.5; HRMS (ESI) m/z calcd. for $C_{34}H_{29}O_6$ $[M+H]^+$: 533.1959, found: 533.1959.



4-(N,N-dipropylsulfamoyl)phenyl-4-((6R,10S)-10-(4-methoxyphenyl)-7-methyl-6-phenyl-6H,10H-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]furo[3,4-e]oxepin-9-yl) benzoate (3uj)

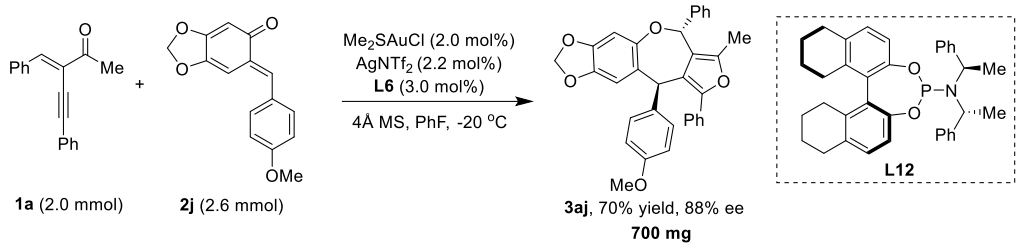
According to general procedure 2: White solid, m.p. = 102-104 ℃; 56 mg, 71% yield; 86% ee; $[\alpha]_D^{20.0}$ = -73.0 (0.1, CH_2Cl_2); [Daicel Chiralpak IA-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 95/5, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) = 21.8 min, t (minor) =16.5 min]**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.3 Hz, 6H), 1.55-1.60 (m, 4H), 1.83 (s, 3H), 3.14 (t, *J* = 7.3 Hz, 4H), 3.78 (s, 3H), 5.11 (s, 1H), 5.59 (s, 1H), 5.82 (s, 2H), 6.27 (s, 1H), 6.81 (s, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 7.08 (s, 2H), 7.19-7.30 (m, 7H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.2 Hz, 2H), 8.33 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.3, 13.0, 22.0, 45.2, 50.0, 55.3, 78.6, 101.2, 107.7, 109.0, 113.8, 120.2, 120.8, 121.9, 127.2, 127.3, 128.1, 128.2, 128.7, 129.4, 129.5, 130.9, 131.8, 132.8, 135.7, 138.7, 143.8, 145.1, 146.3, 146.4, 147.0, 147.7, 149.7, 158.0, 163.9; HRMS (ESI) m/z calcd. for $C_{46}H_{44}NO_9S$ $[M+H]^+$: 786.2731, found: 786.2727.

4. Large-scale reaction and synthetic transformations



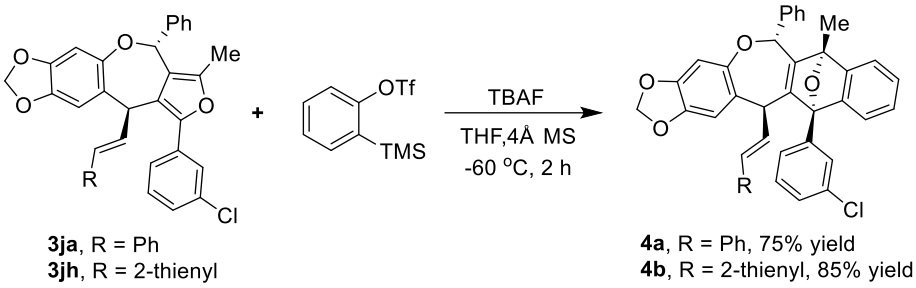
Under nitrogen atmosphere, a solution of **L12** (0.06 mmol, 33.4 mg, 3.0 mol%) and Me_2SAuCl (0.04 mmol, 11.8 mg, 2.0 mol%) in DCE (2.0 mL) was stirred at room temperature for 2 h, then the solvent was removed in vacuum. Next, the $AgNTf_2$ (0.044 mmol, 17.0 mg, 2.2 mol%) was added to the residue and DCE (10 mL) was added, and the mixture was stirred at room temperature for 15 min. Then the precipitate was removed and the remaining solution was transferred into a solution of ketone substrate **1j** (2.0 mmol, 560 mg, 1.0 equiv.) and *ortho* quinone methides **2a** (2.6 mmol, 654 mg

1.3 equiv.) with 4 Å molecular sieves 6 g in DCE (10 mL) at room temperature. Once the reaction was complete as indicated by TLC, the solvent was removed under reduced pressure, and the residue was purified by a silica gel column using ethyl acetate/ petroleum ether=1/60 as the eluent to give aim product **3ja** as white solid. (920 mg, 1.72 mmol) with 87% yield and 93% ee. [Daicel CHIRALPAK® IA-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) = 8.7 min, t (minor) =8.1 min].



Under nitrogen atmosphere, a solution of **L12** (0.06 mmol, 33.4 mg, 3.0 mol%) and Me_2SAuCl (0.04 mmol, 11.8 mg, 2.0 mol%) in DCE (2.0 mL) was stirred at room temperature for 2 h, then the solvent was removed in vacuum. Next, the $AgNTf_2$ (0.044 mmol, 17.0 mg, 2.2 mol%) was added to the residue and PhF (10 mL) was added, and the mixture was stirred at room temperature for 15 min. Then the precipitate was removed and the remaining solution was transferred into a solution of ketone substrate **1a** (2.0 mmol, 492 mg, 1.0 equiv.) and *ortho* quinone methides **2j** (2.6 mmol, 664 mg 1.3 equiv.) with 4 Å molecular sieves 6 g in PhF (10 mL) at room temperature. Once the raw materials were used up, the solvent was removed under reduced pressure, and the residue was purified by a silica gel column using ethyl acetate/ petroleum ether=1/40 as the eluent to give aim product **3aj** as white solid. (700 mg, 1.4 mmol) with 70% yield and 88% ee. [Daicel CHIRALPAK® IA-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 95/5, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) = 11.2 min, t (minor) =7.2 min].

Synthetic procedures for chemical transformations:



3ja, R = Ph
3jh, R = 2-thienyl

4a, R = Ph, 75% yield
4b, R = 2-thienyl, 85% yield

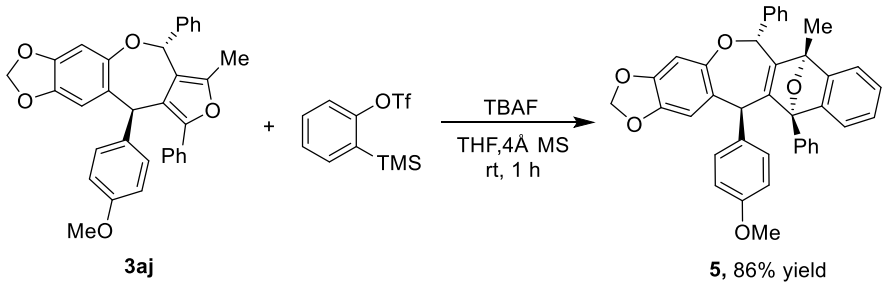
TBAF (0.6 mL, 0.1 mol/L in THF) was slowly added dropwise to a stirred solution of 4 Å MS (60 mg), chiral product (0.1 mmol) and the triflate (0.6 mmol) in dry THF (2.0 mL) at -60 ºC under nitrogen. After stirring for 2 h, the solution was quenched with saturated ammonium chloride and extracted with ethyl acetate. The combined organic phase was dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash chromatography on silica gel with PE/EA=1/30 to afford product **4**.

(6R,7R,12S,13S)-12-(3-chlorophenyl)-7-methyl-6-phenyl-13-((E)-styryl)-6,7,12,13-tetrahydro-7,12-epoxy[1,3]dioxolo[4',5':4,5]benzo[1,2-b]naphtha[2,3-e]oxepine (4a)

White solid, m.p. = 78-80 ℃; 46 mg, 75% yield; $[\alpha]_D^{20.0}$ = -26.9 (0.1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42 (s, 3H), 4.03 (s, 1H), 5.56 (s, 1H), 5.62 (s, 1H), 5.73 (s, 1H), 5.76 (s, 1H), 5.95 (s, 1H), 5.96 (s, 1H), 6.46 (s, 1H), 6.97 (t, J = 7.4 Hz, 1H), 7.05 (d, J = 7.2 Hz, 2H), 7.12 (t, J = 7.3 Hz, 1H), 7.17 (d, J = 7.0 Hz, 1H), 7.19-7.27 (m, 5H), 7.27-7.35 (m, 4H), 7.43-7.54 (m, 2H), 7.71 (d, J = 7.3 Hz, 1H), 7.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.8, 47.1, 80.5, 88.5, 93.0, 101.3, 106.9, 108.2, 118.3, 120.4, 125.1, 125.3, 125.4, 126.6, 127.3, 127.4, 128.1, 128.4, 128.5, 128.6, 128.9, 129.2, 129.7, 130.0, 131.1, 134.8, 136.6, 136.9, 137.3, 143.9, 146.4, 147.8, 149.7, 150.6, 151.0, 151.4; HRMS (ESI) m/z calcd. for $C_{40}H_{30}ClO_4$ $[M+H]^+$:609.1827, found:609.1829.

(6R,7R,12S,13S)-12-(3-chlorophenyl)-7-methyl-6-phenyl-13-((E)-2-(thiophen-2-yl)vinyl)-6,7,12,13-tetrahydro-7,12-epoxy[1,3]dioxolo[4',5':4,5]benzo[1,2-b]-naphtho[2,3-e]oxepine (4b)

White solid, m.p. = 78-80 °C; 52 mg, 85% yield; $[\alpha]_D^{20.0}$ = -42.8 (0.1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42 (s, 3H), 3.99 (d, J = 7.5 Hz, 1H), 5.56 (s, 1H), 5.63 (s, 1H), 5.75 (d, J = 8.2 Hz, 2H), 5.80 (dd, J = 7.8, 15.6 Hz, 1H), 5.96 (d, J = 15.6 Hz, 1H), 6.45 (s, 1H), 6.64 (d, J = 3.4 Hz, 1H), 6.85-6.91 (m, 1H), 7.00 (t, J = 7.4 Hz, 1H), 7.07 (d, J = 5.0 Hz, 1H), 7.12 (t, J = 7.3 Hz, 1H), 7.19-7.34 (m, 7H), 7.43-7.53 (m, 2H), 7.70 (d, J = 7.4 Hz, 1H), 7.82 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.8, 46.6, 80.4, 88.5, 93.0, 101.3, 106.9, 108.2, 118.3, 120.4, 124.2, 124.4, 125.2, 125.3, 125.4, 125.6, 127.1, 127.2, 127.3, 128.4, 128.5, 128.6, 129.2, 129.7, 130.0, 134.9, 136.5, 137.2, 142.0, 143.9, 146.4, 147.9, 150.0, 150.3, 150.9, 151.3; HRMS (ESI) m/z calcd. for $C_{38}H_{28}ClO_4S$ $[M+H]^+$:615.1391, found: 615.1391.

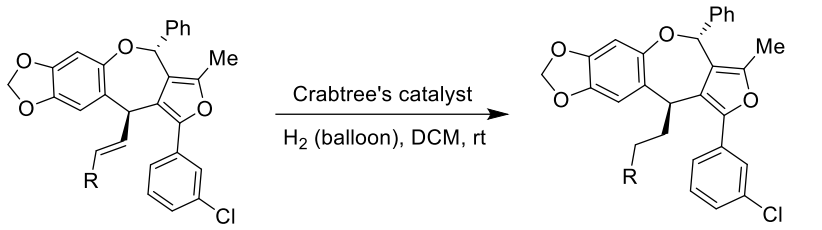


TBAF (0.6 mL, 0.3 mmol in THF) was slowly added dropwise to a stirred solution of 4 Å MS (60 mg), chiral furan **3aj** (0.1 mmol, 50 mg) and the triflate (0.6 mmol) in dry THF (2.0 mL) at room temperature under nitrogen. After stirring for 1 h, the solution was quenched with saturated ammonium chloride and extracted with ethyl acetate. The combined organic phase was dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash chromatography on silica gel with PE/EA=1/20 to afford aim product **5** as white solid (50 mg, 86% yield).

(6R,7R,12S,13S)-13-(4-methoxyphenyl)-7-methyl-6,12-diphenyl-6,7,12,13-tetra-hydro-7,12-epoxy[1,3]dioxolo[4',5':4,5]benzo[1,2-b]naphtho[2,3-e]oxepine (5)

White solid, m.p. = 98-100 °C; 50 mg, 86% yield; $[\alpha]_D^{20.0}$ = -4.4 (0.1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (s, 3H), 3.71 (s, 3H), 4.45 (s, 1H), 5.57 (s, 1H), 5.67 (s, 1H), 5.69 (s, 1H), 5.72 (s, 1H), 6.51 (s, 1H), 6.55 (d, J = 8.6 Hz, 2H), 6.69 (d, J = 8.6 Hz, 2H), 6.78-6.88 (m, 3H), 7.06 (t, J = 7.2 Hz, 1H), 7.25-7.35 (m, 4H), 7.42-7.50 (m, 4H),

7.54 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.9, 48.7, 55.3, 80.5, 88.3, 93.6, 101.2, 106.9, 108.3, 113.7, 117.8, 120.3, 124.7, 125.1, 126.2, 126.8, 128.1, 128.4, 128.5, 129.1, 129.5, 129.8, 130.8, 131.9, 135.1, 136.7, 143.7, 146.1, 147.3, 149.7, 151.1, 151.3, 158.4; HRMS (ESI) m/z calcd. for $C_{39}H_{31}O_5$ $[M+H]^+$: 579.2166, found: 579.2167.



3ja, R = Ph
3jh, R = 2-thienyl

6a, R = Ph, 85% yield
6b, R = 2-thienyl, 86% yield

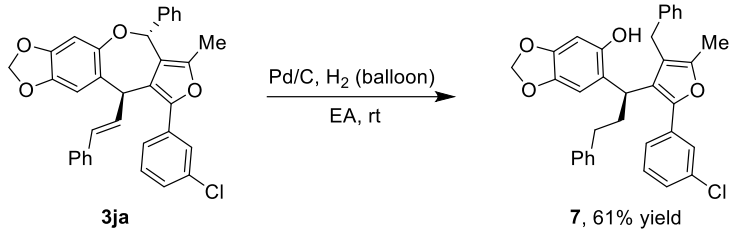
A stirred solution of chiral product (0.1 mmol) in DCM (4.0 mL) was added Crabtree's catalyst (10%, 8 mg) at room temperature and the reaction mixture was stirred for 48 h under H_2 atmosphere. Subsequently, the solvent was evaporated in vacuo. The residue was purified by flash chromatography with PE/EA=1/40 to afford aim product **6**.

(6R,10S)-9-(3-chlorophenyl)-7-methyl-10-phenethyl-6-phenyl-6H,10H-[1,3] dioxolo[4',5':4,5]benzo[1,2-b]furo[3,4-e]oxepine (6a)

Colorless oil, 46 mg, 86% yield; $[\alpha]_D^{20.0}$ = -161.1 (0.1, CH_2Cl_2);^{1}H NMR (400 MHz, $CDCl_3$) δ 1.77 (s, 3H), 2.16-2.26 (m, 1H), 2.45-2.55 (m, 1H), 2.58-2.68 (m, 1H), 2.88-3.00 (m, 1H), 3.83 (dd, J = 3.9, 11.0 Hz, 1H), 5.68 (s, 1H), 5.80 (s, 1H), 5.83 (s, 1H), 6.29 (s, 1H), 6.57 (s, 1H), 7.14 - 6.96 (m, 2H), 7.23 -7.16 (m, 6H), 7.22-7.32 (m, 5H), 7.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.7, 34.1, 37.7, 41.1, 78.7, 101.2, 107.3, 109.6, 120.1, 123.5, 124.6, 125.8, 125.9, 126.7, 128.2, 128.5, 128.6, 128.7, 128.9, 129.5, 129.8, 129.9, 133.1, 134.7, 138.9, 141.9, 143.7, 144.0, 146.1, 147.4; HRMS (ESI) m/z calcd. for $C_{34}H_{28}ClO_4$ $[M+H]^+$: 535.1671, found: 535.1676.

(6R,10S)-9-(3-chlorophenyl)-7-methyl-6-phenyl-10-(2-(thiophen-2-yl)ethyl)-6H,10H-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]furo[3,4-e]oxepine (6b)

White solid, 47 mg, 87% yield; $[\alpha]_D^{20.0}$ = -71.1 (0.1, CH_2Cl_2);^{1}H NMR (400 MHz, $CDCl_3$) δ 1.77 (s, 3H), 2.19-2.33 (m, 1H), 2.68-2.84 (m, 2H), 2.93-3.02 (m, 1H), 3.92 (dd, *J* = 4.4, 11.0 Hz, 1H), 5.68 (s, 1H), 5.76 (s, 1H), 5.79 (s, 1H), 6.29 (s, 1H), 6.59 (s, 1H), 6.77 (d, *J* = 3.3 Hz, 1H), 6.89-6.96 (m, 1H), 7.04 (s, 2H), 7.12 (d, *J* = 5.0 Hz, 1H), 7.18-7.30 (m, 6H), 7.57 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.7, 28.1, 37.9, 40.6, 78.6, 101.2, 107.3, 109.5, 120.1, 123.2, 123.7, 124.3, 124.7, 125.9, 126.8, 126.9, 128.1, 128.2, 128.7, 129.4, 129.5, 129.9, 133.1, 134.7, 138.8, 143.7, 144.2, 144.6, 146.2, 147.4; HRMS (ESI) m/z calcd. for $C_{32}H_{26}ClO_4S$ $[M+H]^+$: 541.1235, found: 541.1238.



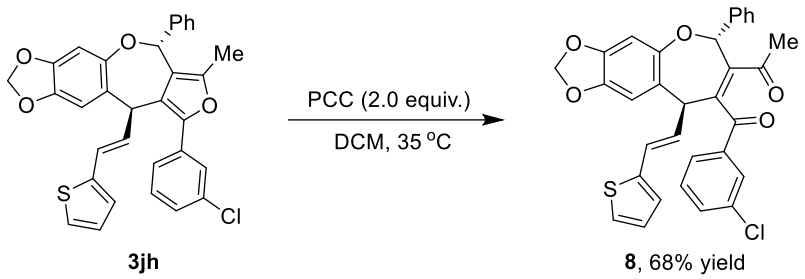
3ja **7**, 61% yield

To a stirred solution of **3ja** (0.1 mmol) in ethyl acetate (4.0 mL), Pd/C (10%, 30 mg) was added and the reaction mixture was stirred at room temperature for 48 h under H_2 atmosphere. Subsequently, it was filtered to remove Pd/C and the solvent was evaporated in vacuo. The residue was purified by silica gel column with hexanes/ethyl acetate (5:1, v/v) to to afford **7** as white solid (38 mg, 71% yield).

(S)-6-(1-(4-benzyl-2-(3-chlorophenyl)-5-methylfuran-3-yl)-3-phenylpropyl)benzo [d][1,3]dioxol-5-ol (7)

Colorless oil, 38 mg, 71% yield; $[\alpha]_D^{20.0}$ = -161.1 (0.1, CH_2Cl_2);^{1}H NMR (400 MHz, $CDCl_3$) δ 1.90-2.04 (m, 1H), 2.15-2.26 (m, 1H), 2.21 (s, 3H), 2.43-2.58 (m, 2H), 3.50 (d, *J* = 16.8 Hz, 1H), 3.64 (d, *J* = 16.8 Hz, 1H), 4.20 (t, *J* = 7.6 Hz, 1H), 4.54 (s, 1H), 5.82 (s, 1H), 5.86 (s, 1H), 6.25 (s, 1H), 6.70 (s, 1H), 6.87 (d, *J* = 7.7 Hz, 2H), 6.95 (d, *J* = 7.5 Hz, 2H), 7.12-7.24 (m, 5H), 7.27-7.35 (m, 3H), 7.45 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 29.6, 33.7, 34.2, 34.7, 99.1, 101.0, 107.0, 118.2, 119.6, 122.2, 125.9, 126.0, 127.3, 127.7, 127.8, 127.9, 128.3, 128.4, 128.5, 128.6, 128.7, 131.0, 139.9, 141.5, 141.6, 146.5, 148.0, 149.4, 150.5; HRMS (ESI) m/z calcd. for $C_{34}H_{30}ClO_4$

$[M+H]^+$: 537.1827, found: 537.1972.



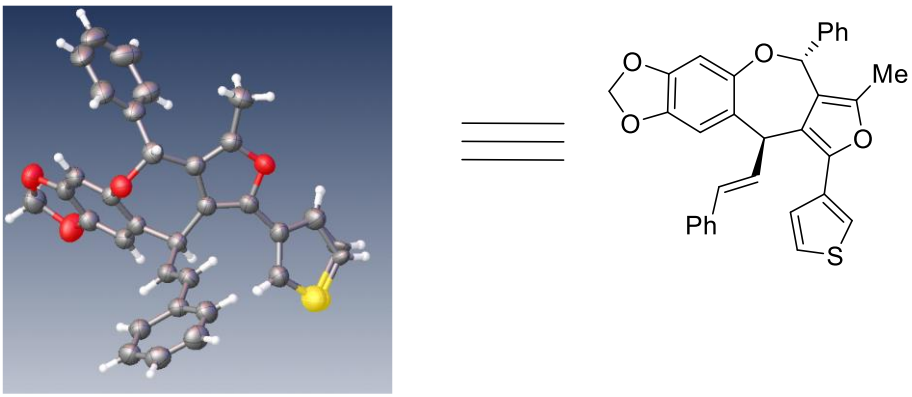
3jh **8**, 68% yield

To a stirred solution of **3jh** (0.1 mmol) in DCM (2.0 mL), PCC (2.0 equiv.) was added and the reaction mixture was stirred at 35°C overnight. Subsequently, it was filtered by silica gel, then the solvent was evaporated in vacuo. The residue was purified by silica gel column with hexanes/ethyl acetate (10:1, v/v) to to afford **8** as white solid (38 mg, 68% yield).

1-((6R,9S)-8-(3-chlorobenzoyl)-6-phenyl-9-((E)-2-(thiophen-2-yl)vinyl)-6,9-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]oxepin-7-yl)ethan-1-one (8)

White solid, m.p. = 128-130℃; 38 mg, 68% yield; $[\alpha]_D^{20.0}$ = -51.1 (0.1, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 1.89 (s, 3H), 4.11 (d, J = 7.8 Hz, 1H), 5.80 (s, 1H), 5.81 (s, 1H), 5.85 (s, 1H), 6.36-6.42 (m, 2H), 6.48 (dd, J = 7.9, 15.5 Hz, 1H), 6.55 (s, 1H), 6.83 (d, J = 3.1 Hz, 1H), 6.86 - 6.90 (m, 1H), 7.10 (d, J = 4.9 Hz, 1H), 7.16 (d, J = 5.7 Hz, 2H), 7.28-7.32 (m, 3H), 7.41 (t, J = 7.8 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 7.7 Hz, 1H), 7.93 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.1, 50.6, 80.5, 101.5, 106.1, 107.9, 124.5, 125.2, 126.1, 126.7, 127.2, 127.3, 128.1, 128.9, 129.0, 129.4, 129.6, 130.2, 133.2, 135.3, 135.6, 137.8, 140.2, 141.5, 144.5, 147.2, 147.3, 147.6, 197.1, 199.2; HRMS (ESI) m/z calcd. for $C_{32}H_{24}ClO_5S$ $[M+H]^+$: 555.1027, found: 555.1027.

5. X-ray Crystallography data



X-ray crystal structure analysis of **3oa** (210625A_auto)

210625A_auto

Table S5 Crystal data and structure refinement for 210625A_auto.

Identification code	210625A_auto
Empirical formula	$C_{32}H_{24}O_4S$
Formula weight	504.57
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	10.4684(3)
b/Å	10.4701(3)
c/Å	12.0220(3)
α/°	102.237(2)
β/°	93.776(2)
γ/°	97.639(2)
Volume/Å^3	1270.28(6)
Z	2
ρ_{calc}g/cm^3	1.319
μ/mm^{-1}	1.429

F(000)	528.0
Crystal size/mm^3	0.06 × 0.06 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.56 to 134.118
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -14 ≤ l ≤ 14
Reflections collected	35351
Independent reflections	4536 [R_{int} = 0.0660, R_{sigma} = 0.0400]
Data/restraints/parameters	4536/24/353
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0447, wR_2 = 0.1198
Final R indexes [all data]	R_1 = 0.0592, wR_2 = 0.1293
Largest diff. peak/hole / e $Å^{-3}$	0.28/-0.38

Table S6 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 210625A_auto. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	4962(13)	1951(14)	1144(11)	80.7(19)
S1A	4753(3)	1786(2)	931(2)	63.6(4)
O1	7654.1(13)	8847.4(13)	4023.7(11)	52.0(3)
O2	4109.6(16)	11288.0(15)	3486.3(14)	67.3(4)
O3	2612.6(15)	9370.2(17)	2993.6(16)	75.5(5)
O4	8025.8(14)	5595.2(14)	830.5(11)	56.1(4)
C1	5501.8(18)	7766.5(18)	3341.7(14)	44.1(4)
C2	8648.4(19)	9853(2)	2591.8(19)	54.6(5)
C3	5986(2)	3364(2)	-113.4(18)	64.9(6)
C4	7000.5(18)	6330.6(18)	2366.5(15)	45.2(4)
C5	5215(18)	2243(13)	-390(11)	50.3(18)
C5A	5172(16)	2027(11)	-203(10)	47(2)
C6	6379.3(19)	8935.1(19)	3687.6(15)	45.8(4)

C7	9384(2)	11005(2)	3231(2)	73.6(7)
C8	4187.1(19)	7837.5(19)	3114.3(16)	48.6(4)
C9	5639(2)	3247(2)	1733.2(17)	55.3(5)
C10	6345.7(19)	6127.5(19)	4336.2(16)	48.1(4)
C11	8583(2)	4859(2)	7827(2)	64.7(6)
C12	7685.0(19)	5234.6(19)	5700.3(16)	47.6(4)
C13	8029(2)	9884(2)	1552(2)	69.1(6)
C14	5970.0(18)	6434.0(18)	3192.2(15)	45.2(4)
C15	8847(3)	12175(3)	1809(4)	92.4(10)
C16	7026(2)	5293(2)	1475.8(15)	49.1(5)
C17	8491.4(19)	8644(2)	3101.7(17)	52.0(5)
C18	4724(2)	10200.5(19)	3500.9(16)	50.5(5)
C19	8615(2)	4431(2)	5796.1(19)	58.5(5)
C20	8049.0(19)	7336.0(19)	2281.0(16)	47.7(4)
C21	7645(2)	5640(2)	7750.3(18)	59.7(5)
C22	7296(2)	5501(2)	4575.6(16)	51.4(5)
C23	9059(2)	4246(2)	6854(2)	65.8(6)
C24	7193(2)	5823(2)	6698.8(16)	52.4(5)
C25	2771(2)	10780(2)	3215(2)	68.5(6)
C26	6235(2)	4004.5(19)	1060.6(16)	50.0(4)
C27	9745(2)	7380(3)	781(2)	69.9(6)
C28	6003(2)	10181.0(19)	3767.3(16)	50.1(5)
C29	8128(3)	11053(3)	1159(3)	86.4(8)
C30	8634(2)	6845(2)	1342.7(17)	54.1(5)
C31	9479(3)	12165(3)	2837(3)	91.9(10)
C32	3830.6(19)	9064(2)	3199.5(16)	50.8(5)

Table S7 Anisotropic Displacement Parameters ($Å^2×10^3$) for 210625A_auto. The Anisotropic displacement factor exponent takes the form: -$2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	92(4)	75(3)	64(3)	3(3)	11(3)	-4(3)
S1A	76.1(9)	49.8(7)	56.7(9)	2.0(6)	11.8(6)	-6.2(5)
O1	55.8(8)	52.7(8)	44.0(7)	6.6(6)	1.3(6)	3.8(6)
O2	77.0(10)	49.7(9)	80.5(10)	15.1(7)	18.0(8)	22.5(8)
O3	60.3(9)	63.0(10)	103.8(13)	14.4(9)	6.2(8)	19.3(8)
O4	71.9(9)	52.5(8)	43.8(7)	9.5(6)	16.8(6)	5.7(7)
C1	55.4(11)	40.8(10)	35.7(9)	6.9(7)	6.1(7)	7.1(8)
C2	44.5(10)	50.2(12)	67.8(13)	11.8(10)	13.2(9)	0.9(8)
C3	89.4(15)	58.0(13)	43.1(10)	9.0(9)	9.4(10)	-1.5(11)
C4	55.2(11)	43.3(10)	38.4(9)	11.1(8)	6.2(8)	8.4(8)
C5	80(3)	49(4)	23(3)	18(3)	13(2)	-7(3)
C5A	73(3)	31(4)	31(5)	10(3)	2(3)	-12(3)
C6	54.9(11)	44.0(11)	37.2(9)	7.3(8)	5.4(8)	5.1(8)
C7	66.5(14)	62.4(15)	82.4(16)	1.9(12)	21.3(12)	-8.9(11)
C8	54.8(11)	43.9(11)	46.0(10)	8.1(8)	7.8(8)	5.3(8)
C9	69.4(12)	50.6(11)	45.0(10)	7.2(8)	11.5(9)	8.6(9)
C10	59.9(11)	42.8(11)	43.9(10)	11.6(8)	13.7(8)	8.4(9)
C11	73.7(14)	65.3(14)	56.4(12)	22.7(11)	-1.9(10)	4.7(11)
C12	52.4(10)	43.7(10)	47.8(10)	12.8(8)	9.8(8)	4.1(8)
C13	61.1(13)	62.7(15)	86.2(16)	28.1(12)	6.0(12)	1.1(11)
C14	51.3(10)	39.2(10)	43.9(10)	8.1(8)	6.3(8)	4.1(8)
C15	92(2)	62.2(18)	138(3)	39.6(19)	59(2)	13.1(15)
C16	62.3(12)	48.4(11)	39.3(9)	13.0(8)	11.4(8)	9.8(9)
C17	48.7(10)	53.2(12)	51.1(11)	7.4(9)	2.9(8)	5.0(9)
C18	69.4(13)	42.7(11)	43.4(10)	10.3(8)	16.1(9)	15.7(9)
C19	61.3(12)	58.8(13)	60.5(12)	16.4(10)	16.4(10)	17.3(10)
C20	54.3(11)	45.4(11)	44.6(10)	13.2(8)	4.7(8)	6.3(8)
C21	75.9(14)	55.5(13)	48.5(11)	13.7(9)	9.7(10)	7.5(11)
C22	59.3(12)	52.5(12)	45.5(10)	12.4(9)	15.6(8)	12.3(9)
C23	64.0(13)	65.0(14)	74.6(15)	24.9(12)	3.3(11)	18.1(11)

C24	61.1(12)	48.3(11)	50.9(11)	14.6(9)	11.5(9)	10.1(9)
C25	74.0(15)	65.1(15)	75.4(15)	21.0(12)	18.0(12)	28.9(12)
C26	64.9(11)	43.7(10)	41.3(9)	6.9(8)	8.9(8)	10.3(8)
C27	74.4(15)	72.1(16)	66.3(14)	19.7(12)	25.2(11)	5.8(12)
C28	62.7(12)	41.5(11)	44.2(10)	5.4(8)	12.5(8)	3.8(9)
C29	76.5(17)	88(2)	113(2)	54.6(18)	23.8(15)	17.6(15)
C30	64.3(12)	49.9(12)	47.9(11)	13.0(9)	9.0(9)	3.1(9)
C31	97(2)	51.9(16)	119(3)	3.5(15)	51.3(19)	-13.8(14)
C32	53.9(11)	53.2(12)	47.1(10)	10.3(9)	9.9(8)	13.2(9)

Table S8 Bond Lengths for 210625A_auto.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C5	1.961(17)	C4	C20	1.441(3)
S1	C9	1.455(11)	C6	C28	1.398(3)
S1A	C5A	1.520(11)	C7	C31	1.388(4)
S1A	C9	1.735(3)	C8	C32	1.369(3)
O1	C6	1.389(2)	C9	C26	1.371(3)
O1	C17	1.456(2)	C10	C14	1.516(3)
O2	C18	1.383(2)	C10	C22	1.311(3)
O2	C25	1.422(3)	C11	C21	1.369(3)
O3	C25	1.428(3)	C11	C23	1.368(3)
O3	C32	1.375(2)	C12	C19	1.384(3)
O4	C16	1.386(2)	C12	C22	1.480(3)
O4	C30	1.372(3)	C12	C24	1.392(3)
C1	C6	1.396(3)	C13	C29	1.396(4)
C1	C8	1.400(3)	C15	C29	1.362(5)
C1	C14	1.519(3)	C15	C31	1.365(5)
C2	C7	1.386(3)	C16	C26	1.455(3)
C2	C13	1.378(3)	C17	C20	1.504(3)
C2	C17	1.513(3)	C18	C28	1.360(3)

C3	C5	1.298(14)	C18	C32	1.378(3)
C3	C5A	1.517(11)	C19	C23	1.386(3)
C3	C26	1.419(3)	C20	C30	1.357(3)
C4	C14	1.512(2)	C21	C24	1.381(3)
C4	C16	1.359(3)	C27	C30	1.487(3)

Table S9 Bond Angles for 210625A_auto.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	S1	C5	94.5(9)	C4	C14	C10	114.81(15)
C5A	S1A	C9	94.2(5)	C10	C14	C1	111.45(15)
C6	O1	C17	115.19(14)	C29	C15	C31	120.7(3)
C18	O2	C25	105.61(17)	O4	C16	C26	115.87(16)
C32	O3	C25	105.46(18)	C4	C16	O4	109.64(17)
C30	O4	C16	107.07(15)	C4	C16	C26	134.46(18)
C6	C1	C8	119.20(17)	O1	C17	C2	109.31(16)
C6	C1	C14	120.43(17)	O1	C17	C20	110.93(16)
C8	C1	C14	120.36(17)	C20	C17	C2	116.56(17)
C7	C2	C17	118.5(2)	C28	C18	O2	127.96(19)
C13	C2	C7	118.4(2)	C28	C18	C32	122.40(18)
C13	C2	C17	123.03(19)	C32	C18	O2	109.64(18)
C5	C3	C26	118.3(6)	C12	C19	C23	120.9(2)
C26	C3	C5A	108.2(5)	C4	C20	C17	127.70(16)
C16	C4	C14	125.39(18)	C30	C20	C4	106.73(17)
C16	C4	C20	106.52(16)	C30	C20	C17	125.45(18)
C20	C4	C14	127.77(16)	C11	C21	C24	120.3(2)
C3	C5	S1	99.4(9)	C10	C22	C12	126.65(17)
C3	C5A	S1A	114.1(8)	C11	C23	C19	120.4(2)
O1	C6	C1	118.25(16)	C21	C24	C12	121.1(2)
O1	C6	C28	119.30(17)	O2	C25	O3	108.92(17)
C1	C6	C28	122.35(18)	C3	C26	C16	123.67(18)

C2	C7	C31	120.6(3)	C9	C26	C3	110.97(19)
C32	C8	C1	117.82(19)	C9	C26	C16	125.35(17)
C26	C9	S1	116.2(6)	C18	C28	C6	116.37(19)
C26	C9	S1A	112.17(18)	C15	C29	C13	119.7(3)
C22	C10	C14	126.69(17)	O4	C30	C27	116.29(18)
C23	C11	C21	119.6(2)	C20	C30	O4	110.03(17)
C19	C12	C22	120.10(17)	C20	C30	C27	133.7(2)
C19	C12	C24	117.62(18)	C15	C31	C7	119.9(3)
C24	C12	C22	122.20(18)	O3	C32	C18	110.23(18)
C2	C13	C29	120.8(3)	C8	C32	O3	128.0(2)
C4	C14	C1	110.72(15)	C8	C32	C18	121.77(19)

Table S10 Torsion Angles for 210625A_auto.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	C9	C26	C3	3.6(7)	C14	C1	C6	C28	175.92(16)
S1	C9	C26	C16	-176.2(7)	C14	C1	C8	C32	-176.28(16)
S1A	C9	C26	C3	-1.4(3)	C14	C4	C16	O4	173.49(16)
S1A	C9	C26	C16	178.80(19)	C14	C4	C16	C26	-4.5(3)
O1	C6	C28	C18	-175.56(15)	C14	C4	C20	C17	10.5(3)
O1	C17	C20	C4	-3.5(3)	C14	C4	C20	C30	-173.43(18)
O1	C17	C20	C30	-178.93(18)	C14	C10	C22	C12	178.17(19)
O2	C18	C28	C6	-178.52(17)	C16	O4	C30	C20	-0.2(2)
O2	C18	C32	O3	-0.7(2)	C16	O4	C30	C27	-179.56(18)
O2	C18	C32	C8	178.12(17)	C16	C4	C14	C1	-131.93(19)
O4	C16	C26	C3	-31.3(3)	C16	C4	C14	C10	100.8(2)
O4	C16	C26	C9	148.4(2)	C16	C4	C20	C17	-175.74(19)
C1	C6	C28	C18	0.7(3)	C16	C4	C20	C30	0.4(2)
C1	C8	C32	O3	178.46(18)	C17	O1	C6	C1	86.7(2)
C1	C8	C32	C18	-0.1(3)	C17	O1	C6	C28	-96.85(19)
C2	C7	C31	C15	-0.1(4)	C17	C2	C7	C31	-175.3(2)

C2	C13	C29	C15	0.2(4)	C17	C2	C13	C29	175.0(2)
C2	C17	C20	C4	-129.5(2)	C17	C20	C30	O4	176.12(17)
C2	C17	C20	C30	55.1(3)	C17	C20	C30	C27	-4.7(4)
C4	C16	C26	C3	146.6(2)	C18	O2	C25	O3	-3.9(2)
C4	C16	C26	C9	-33.7(4)	C19	C12	C22	C10	172.7(2)
C4	C20	C30	O4	-0.1(2)	C19	C12	C24	C21	1.8(3)
C4	C20	C30	C27	179.1(2)	C20	C4	C14	C1	40.8(2)
C5	S1	C9	C26	-6.3(10)	C20	C4	C14	C10	-86.5(2)
C5	C3	C26	C9	3.5(9)	C20	C4	C16	O4	-0.5(2)
C5	C3	C26	C16	-176.7(9)	C20	C4	C16	C26	-178.5(2)
C5A	S1A	C9	C26	4.0(6)	C21	C11	C23	C19	1.2(4)
C5A	C3	C26	C9	-1.9(7)	C22	C10	C14	C1	-144.3(2)
C5A	C3	C26	C16	177.9(7)	C22	C10	C14	C4	-17.4(3)
C6	O1	C17	C2	65.9(2)	C22	C12	C19	C23	175.3(2)
C6	O1	C17	C20	-64.0(2)	C22	C12	C24	C21	-174.91(19)
C6	C1	C8	C32	2.6(3)	C23	C11	C21	C24	-0.9(3)
C6	C1	C14	C4	-55.7(2)	C24	C12	C19	C23	-1.5(3)
C6	C1	C14	C10	73.4(2)	C24	C12	C22	C10	-10.7(3)
C7	C2	C13	C29	-0.8(3)	C25	O2	C18	C28	-176.9(2)
C7	C2	C17	O1	71.1(2)	C25	O2	C18	C32	2.8(2)
C7	C2	C17	C20	-162.10(19)	C25	O3	C32	C8	179.6(2)
C8	C1	C6	O1	173.38(15)	C25	O3	C32	C18	-1.7(2)
C8	C1	C6	C28	-2.9(3)	C26	C3	C5	S1	-6.7(12)
C8	C1	C14	C4	123.14(18)	C26	C3	C5A	S1A	5.0(12)
C8	C1	C14	C10	-107.76(19)	C28	C18	C32	O3	179.01(17)
C9	S1A	C5A	C3	-5.0(10)	C28	C18	C32	C8	-2.2(3)
C11	C21	C24	C12	-0.7(3)	C29	C15	C31	C7	-0.5(4)
C12	C19	C23	C11	0.0(4)	C30	O4	C16	C4	0.4(2)
C13	C2	C7	C31	0.7(3)	C30	O4	C16	C26	178.85(16)
C13	C2	C17	O1	-104.7(2)	C31	C15	C29	C13	0.4(4)
C13	C2	C17	C20	22.1(3)	C32	O3	C25	O2	3.4(2)

C14	C1	C6	O1	-7.8(2)	C32	C18	C28	C6	1.8(3)

Table S11 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 210625A_auto.

Atom	*x*	*y*	*z*	U(eq)
H3A	6366.1	3736.71	-671.03	78
H3B	6272.73	3703.81	-722.93	78
H5	4881.17	1730.13	-1104.9	60
H5A	4949.65	1409.65	-891.18	56
H7	9816.88	11001.79	3930.89	88
H8	3576.07	7076.58	2911.96	58
H9A	5665.25	3545.45	2521.42	66
H9B	5701.97	3488.94	2527.48	66
H10	5851.26	6413.4	4929.04	58
H11	8895.05	4746.05	8536.75	78
H13	7540.74	9117.82	1106.78	83
H14	5228.23	5768.54	2831.17	54
H15	8907.21	12955.07	1550.27	111
H17	9348.01	8592.9	3455.77	62
H19	8947.7	4008.57	5141.67	70
H21	7310.51	6048.12	8408.86	72
H22	7774.76	5191.95	3977.22	62
H23	9684.79	3702.46	6903.18	79
H24	6548.59	6347.3	6656.88	63
H25A	2440.71	11058.87	2546.31	82
H25B	2290.12	11115.58	3848.02	82
H27A	10153.2	6665.46	396.8	105
H27B	10359.08	7973.83	1348.97	105
H27C	9438.39	7847.55	236.12	105
H28	6595.67	10954.56	3990.3	60

H29	7704.15	11065.52	457.99	104
H31	9973.81	12934.52	3271.81	110

Table S12 Atomic Occupancy for 210625A_auto.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
S1	0.2	S1A	0.8	H3A	0.5
H3B	0.5	C5	0.5	H5	0.5
C5A	0.5	H5A	0.5	H9A	0.5
H9B	0.5				

Experimental

Single crystals of $C_{32}H_{24}O_4S$ **[210625A_auto]** were crystallized from diethyl ether and *n*-hexane. A suitable crystal was selected on a diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2 [1], the structure was solved with the Unknown [2] structure solution program using Unknown and refined with the Unknown [3] refinement package using Unknown minimisation.

Crystal structure determination of [210625A_auto]

Crystal Data for $C_{32}H_{24}O_4S$ (M =504.57 g/mol): triclinic, space group P-1 (no. 2), a = 10.4684(3) Å, b = 10.4701(3) Å, c =12.0220(3) Å, α =102.237(2)°, β = 93.776(2)°, γ = 97.639(2)°, V = 1270.28(6) Å^3, Z = 2, T = 293(2) K, μ(Cu Kα) = 1.429 mm^{-1}, *Dcalc* = 1.319 g/cm^3, 35351 reflections measured (7.56° ≤ 2Θ ≤ 134.118°), 4536 unique (R_{int} = 0.0660, R_{sigma} = 0.0400) which were used in all calculations. The final R_1 was 0.0447 (I > 2σ(I)) and wR_2 was 0.1293 (all data).

6. References

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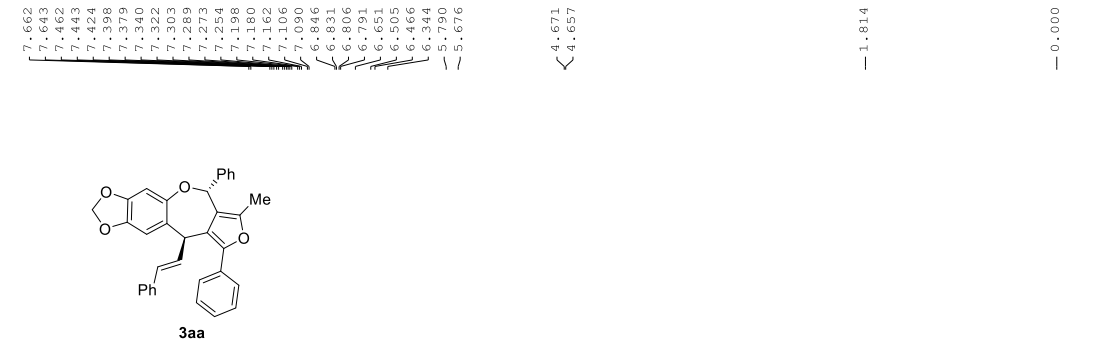
7. NMR Spectra



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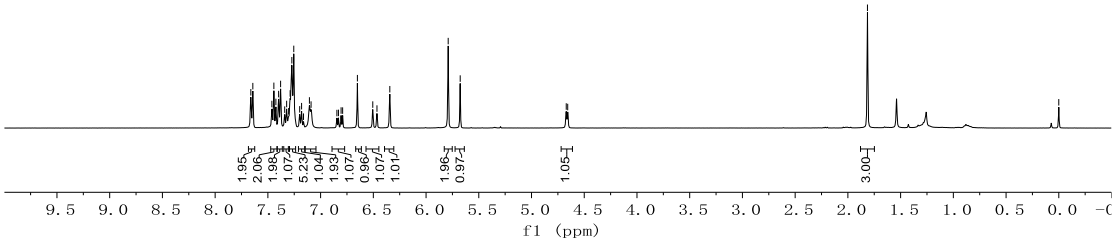

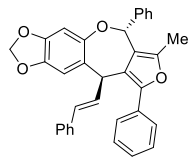

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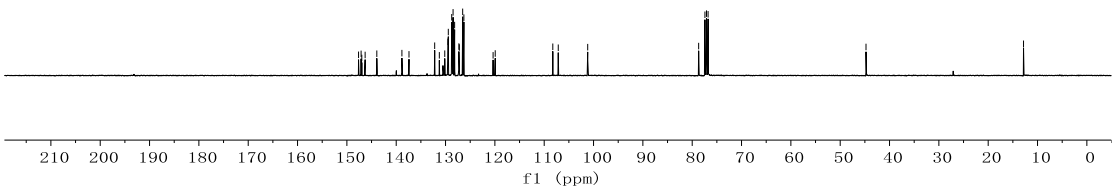

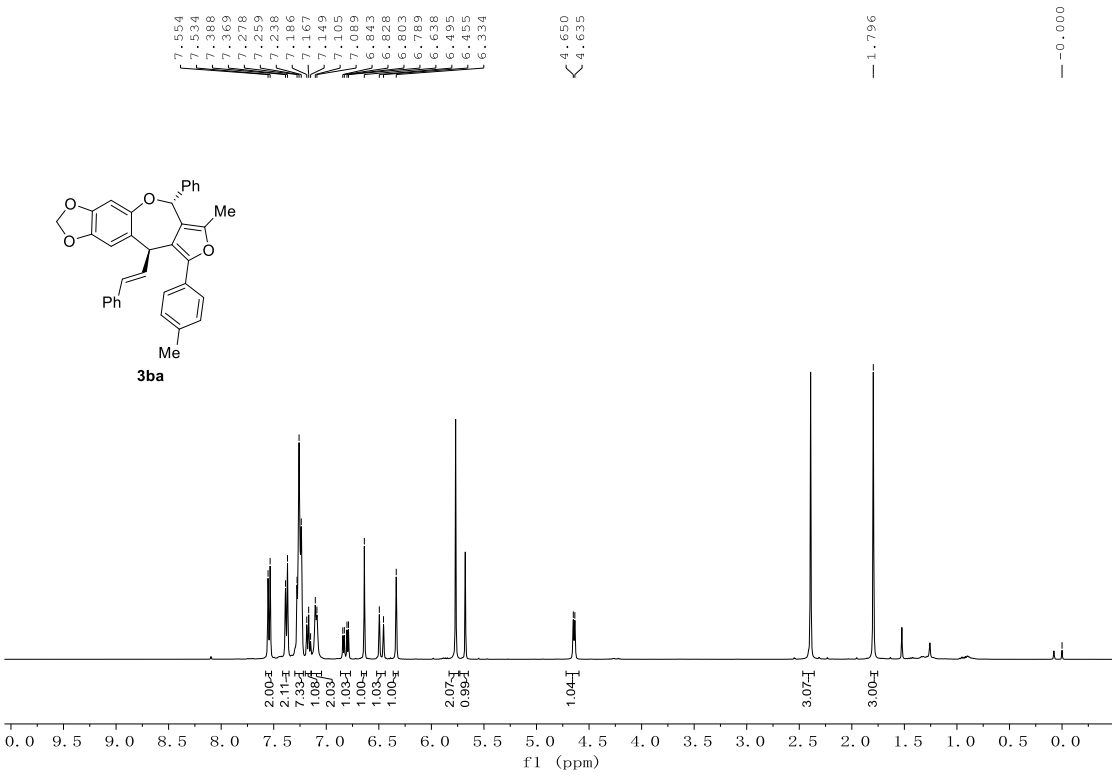
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6.789
6.638
6.495
6.455
6.334
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O
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Ph
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7.33
1.08
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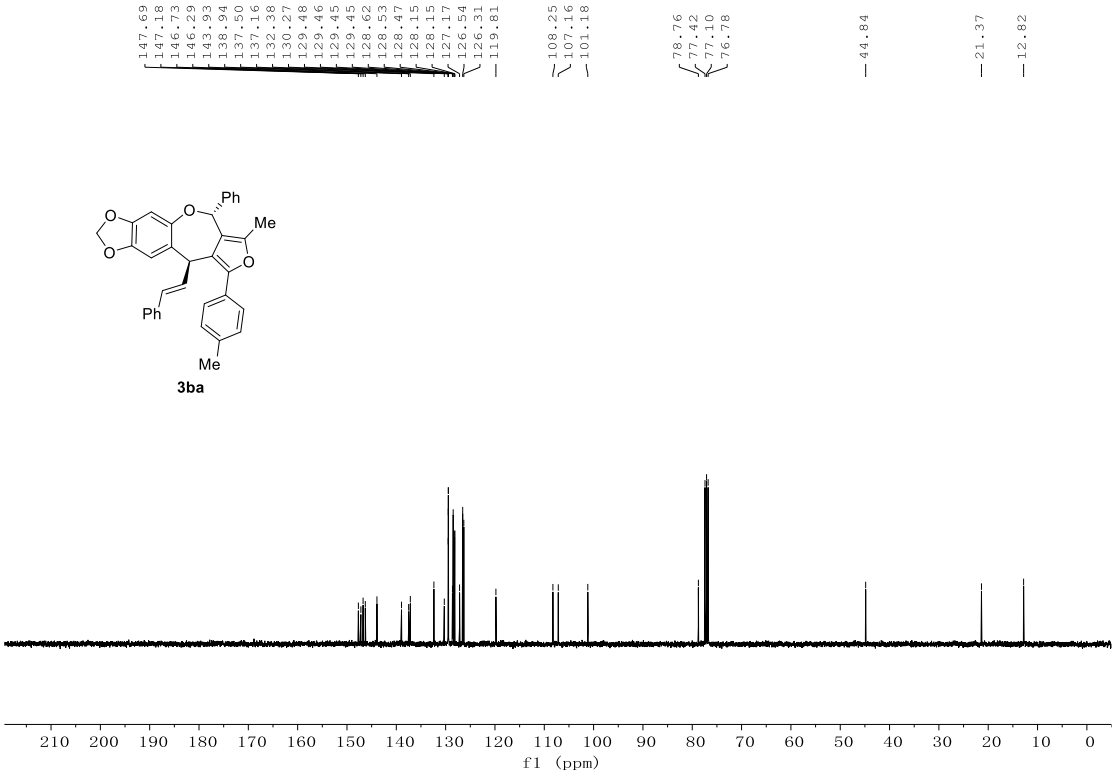
1.03
1.00
1.03
1.00
2.07
0.99
1.04
3.07
3.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.42
77.10
76.78
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21.37
12.82
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O
O
O
Ph
Me
3ba
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f1 (ppm)


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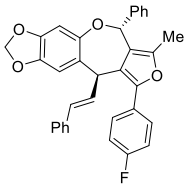
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Ph
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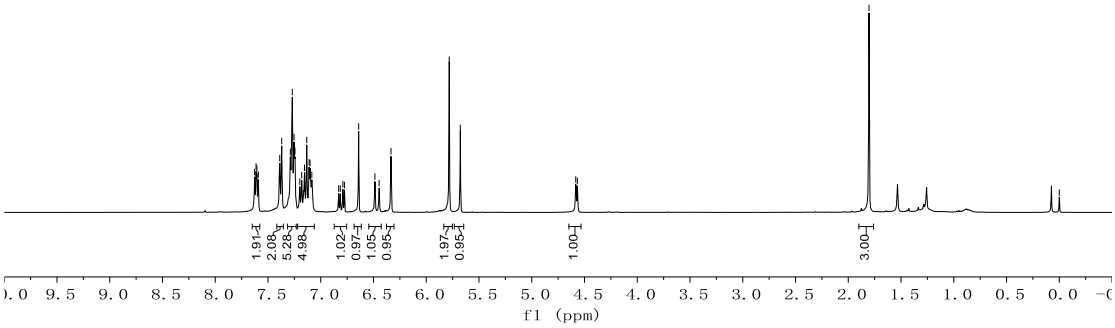
3ca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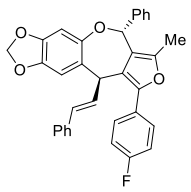
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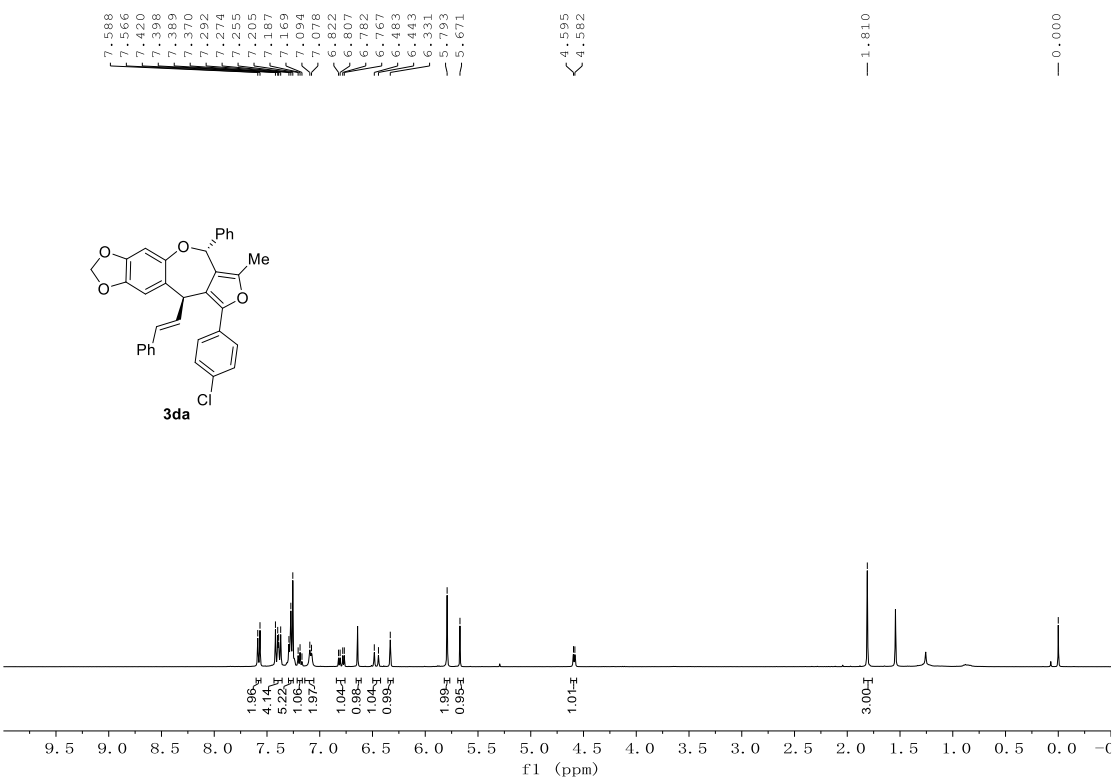
O
O
Me
O
Ph
F

3ca

f1 (ppm)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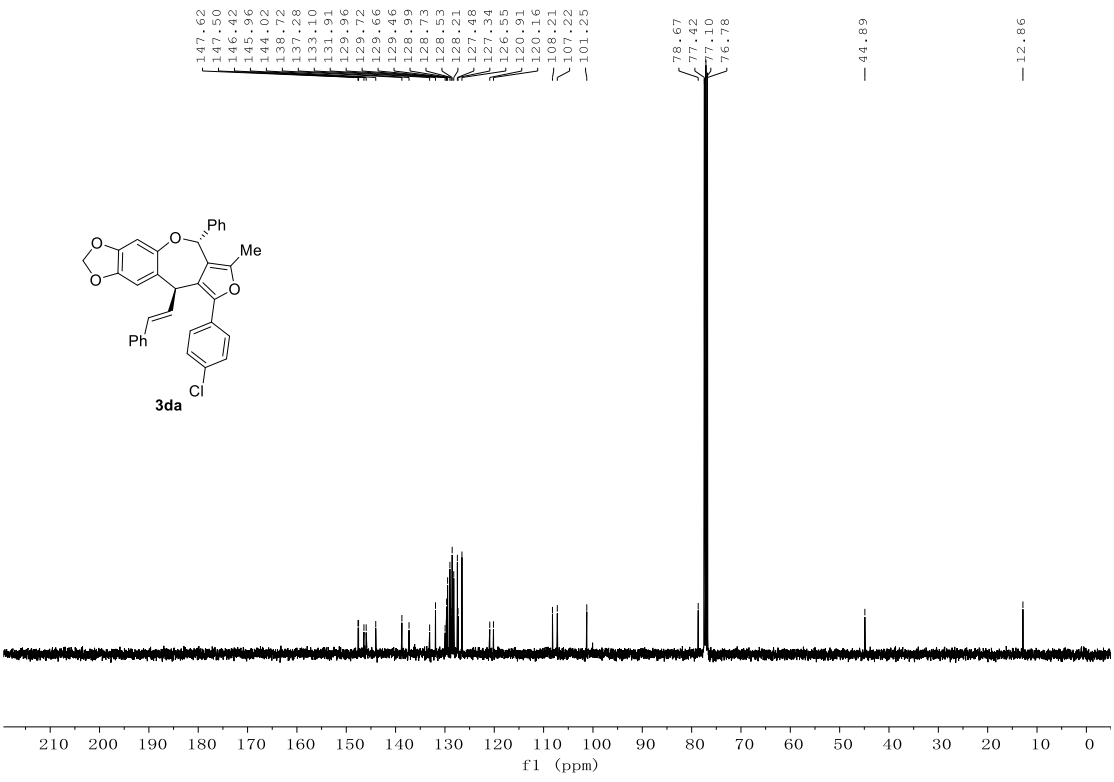
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128.73
128.53
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127.48
127.34
126.55
120.91
120.16
108.21
107.22
101.25
78.67
77.42
77.10
76.78
44.89
12.86
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Me
O
O
O
Ph
Cl
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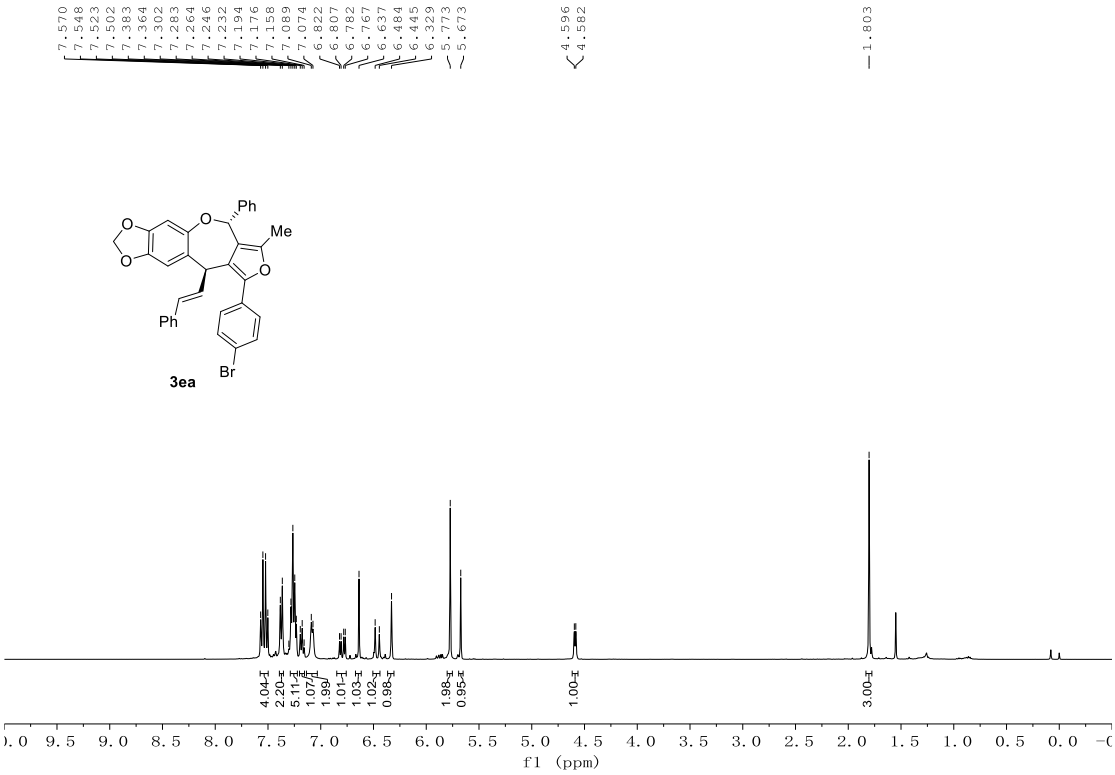
f1 (ppm)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7.176
7.158
7.089
7.074
6.822
6.807
6.782
6.767
6.637
6.484
6.445
6.329
5.773
5.673
4.596
4.582
1.803
Ph
O
O
O
Me
Ph
Br
3ea
4.04
2.20
5.11
1.07
1.99
1.01
1.03
1.02
0.98
1.98
0.95
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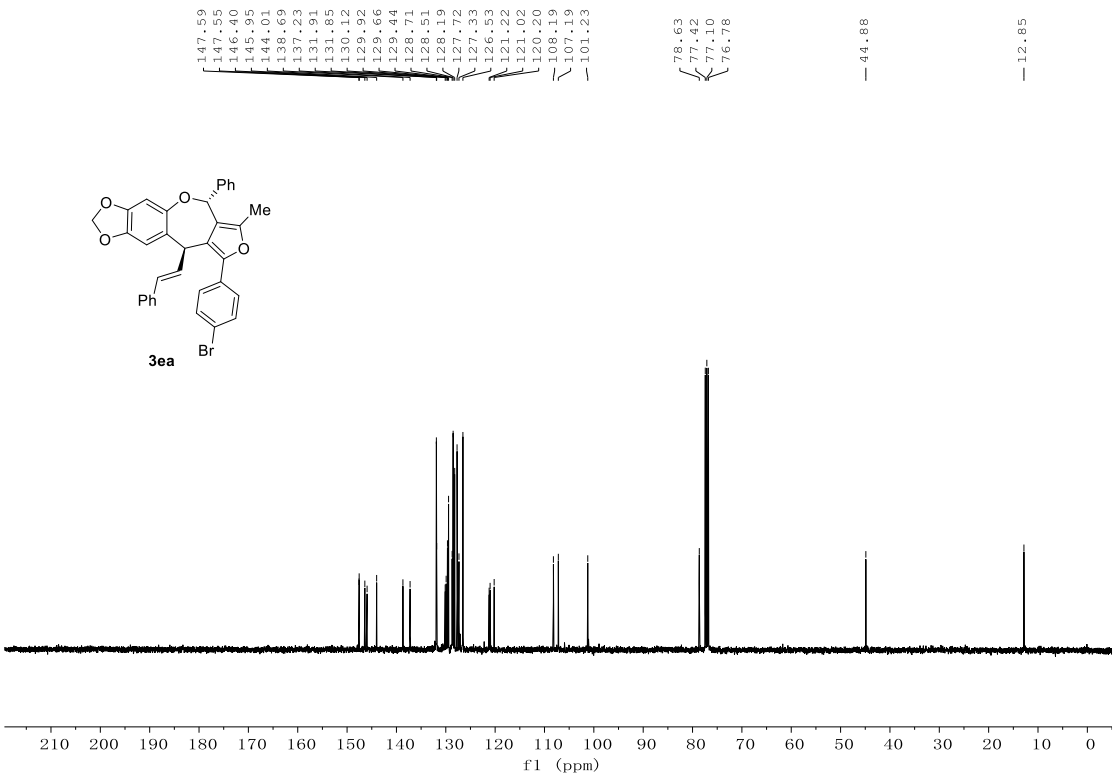
3.00
f1 (ppm)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128.71
128.51
128.19
127.72
127.33
126.53
121.22
121.02
120.20
108.19
107.19
101.23
78.63
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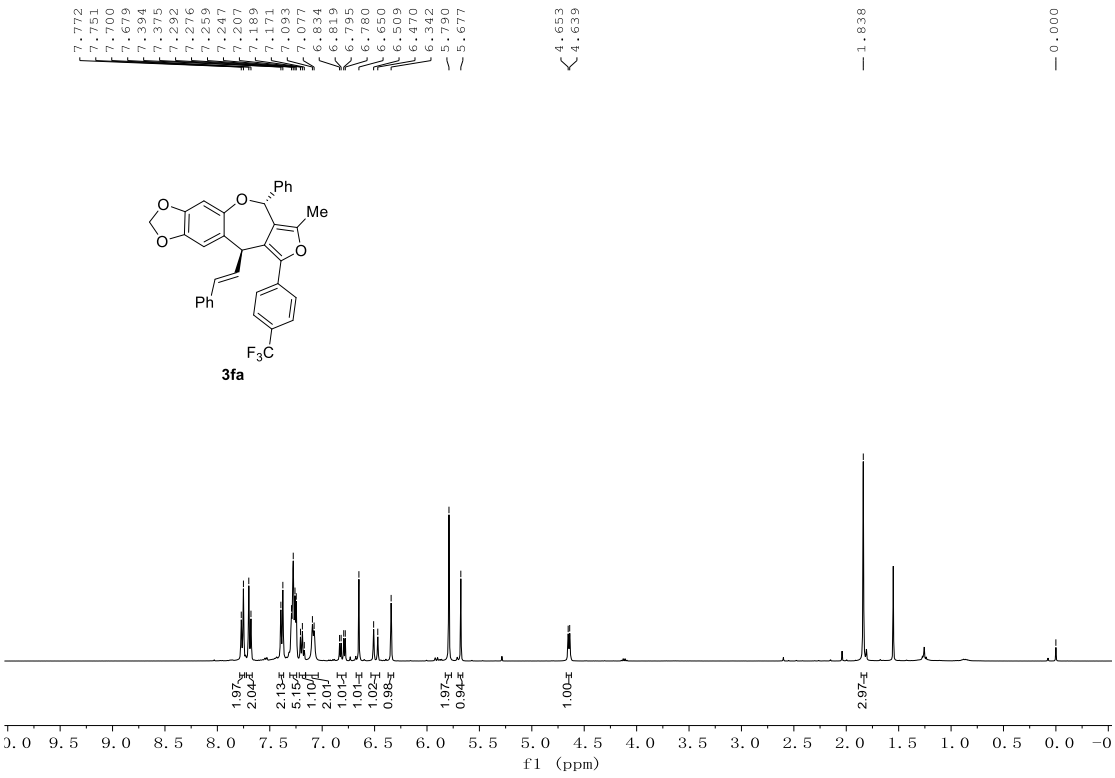
76.78
44.88
12.85
Ph
O
O
O
Me
Ph
Br
3ea
f1 (ppm)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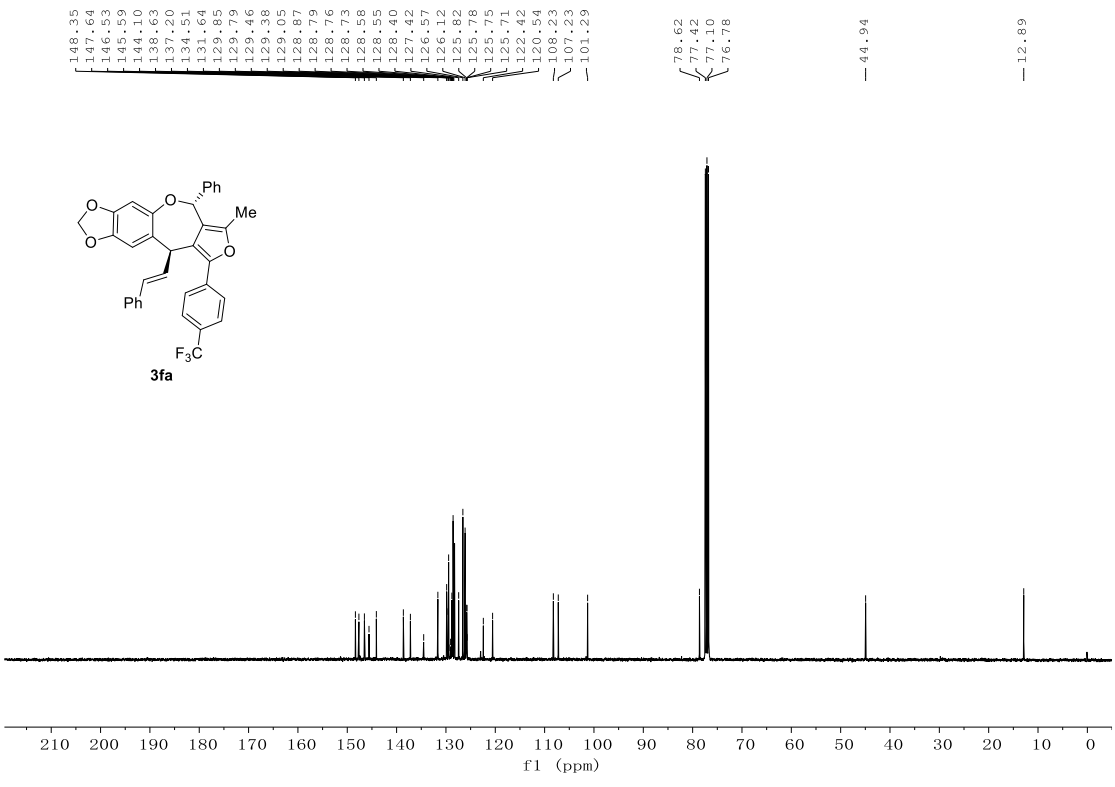
7.171
7.093
7.077
6.834
6.819
6.795
6.780
6.650
6.509
6.470
6.342
5.790
5.677
4.653
4.639
1.838
0.000
Ph
Me
O
O
O
Ph
F3C
1.97
2.04
2.13
5.15
1.10
2.01
1.01
1.01
1.02
0.98
1.97
0.94
1.00
2.97
f1 (ppm)

3fa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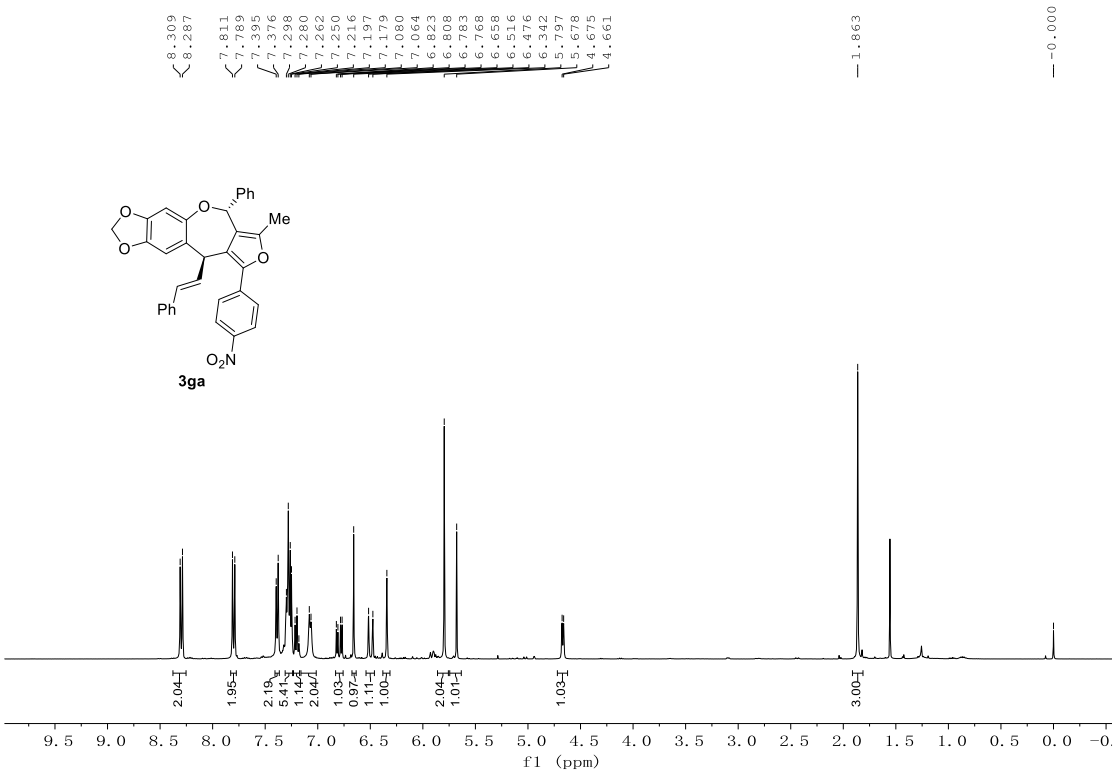
129.38
129.05
128.87
128.79
128.76
128.73
128.58
128.55
128.40
127.42
126.57
126.12
125.82
125.78
125.75
125.71
122.42
120.54
108.23
107.23
101.29
78.62
77.42
77.10
76.78
44.94
12.89
Ph
Me
O
O
O
Ph
F3C
f1 (ppm)

3fa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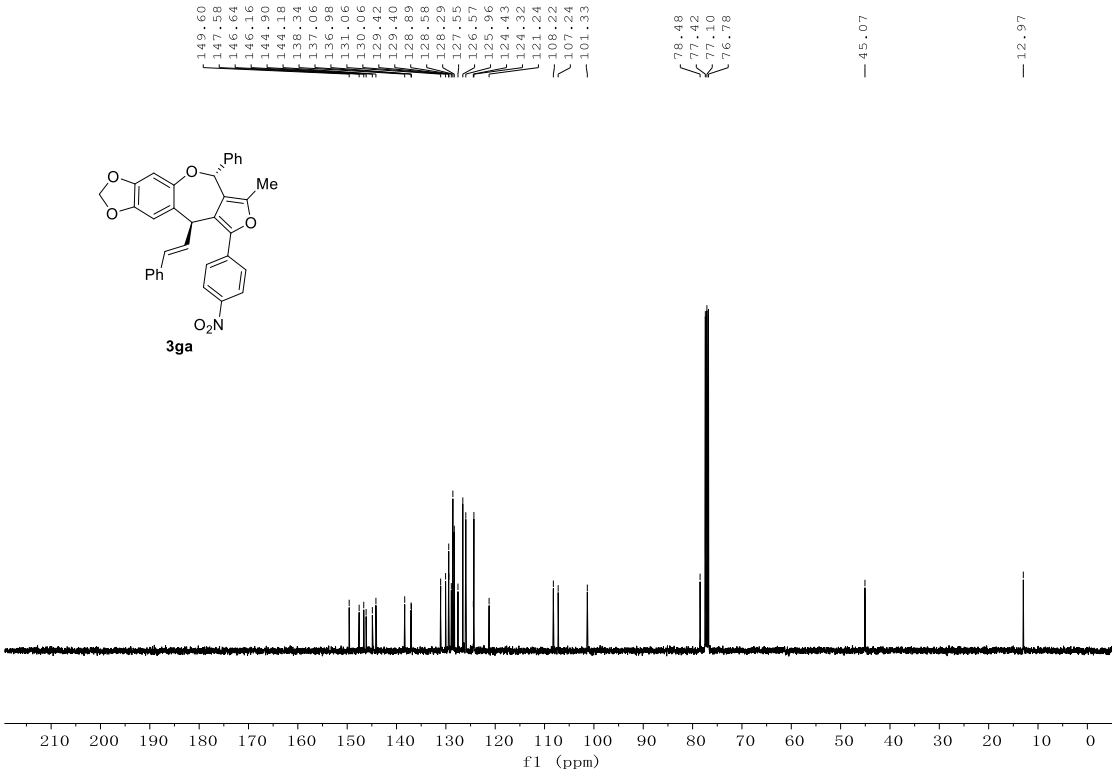
7.280
7.262
7.250
7.216
7.197
7.179
7.080
7.064
6.823
6.808
6.783
6.768
6.658
6.516
6.476
6.342
5.797
5.678
4.675
4.661
1.863
-0.000
Ph
Me
O
O
O
Ph
O2N
3ga
2.04
1.95
2.19
5.41
1.14
2.04
1.03
0.97
1.11
1.00
2.04
1.01
1.03
3.00
f1 (ppm)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137.06
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131.06
130.06
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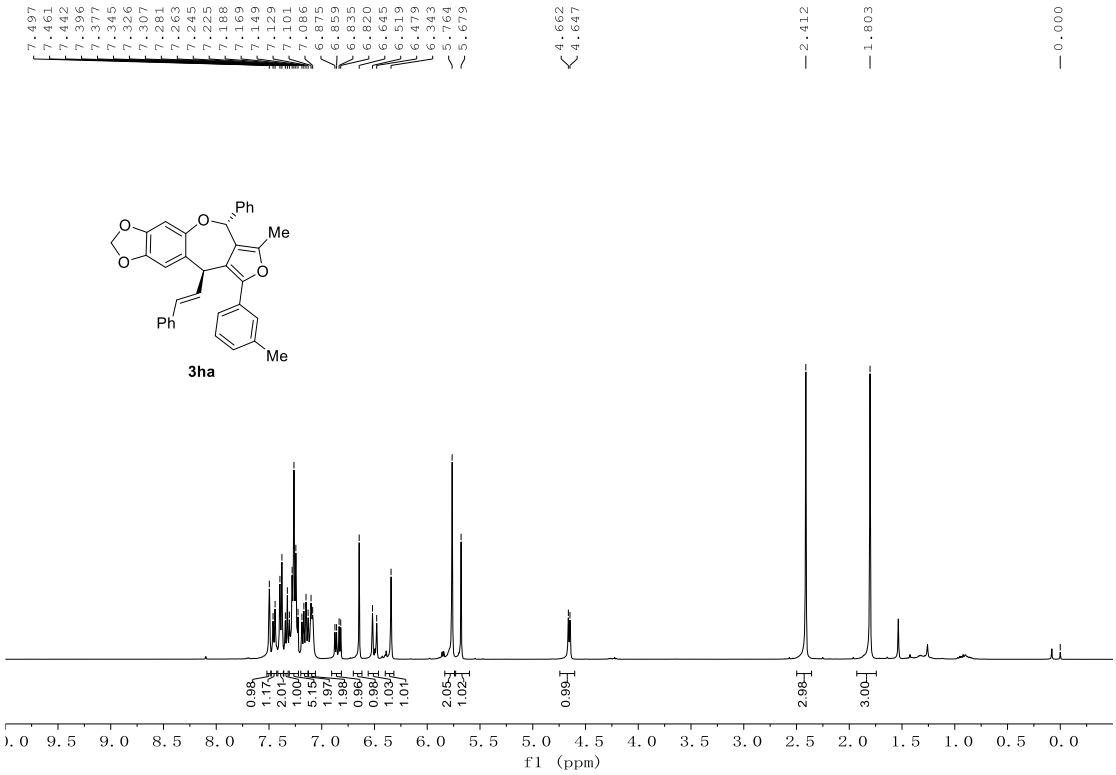
129.40
128.89
128.58
128.29
127.55
126.57
125.96
124.43
124.32
121.24
108.22
107.24
101.33
78.48
77.42
77.10
76.78
45.07
12.97
Ph
Me
O
O
O
Ph
O2N
3ga
f1 (ppm)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7.307
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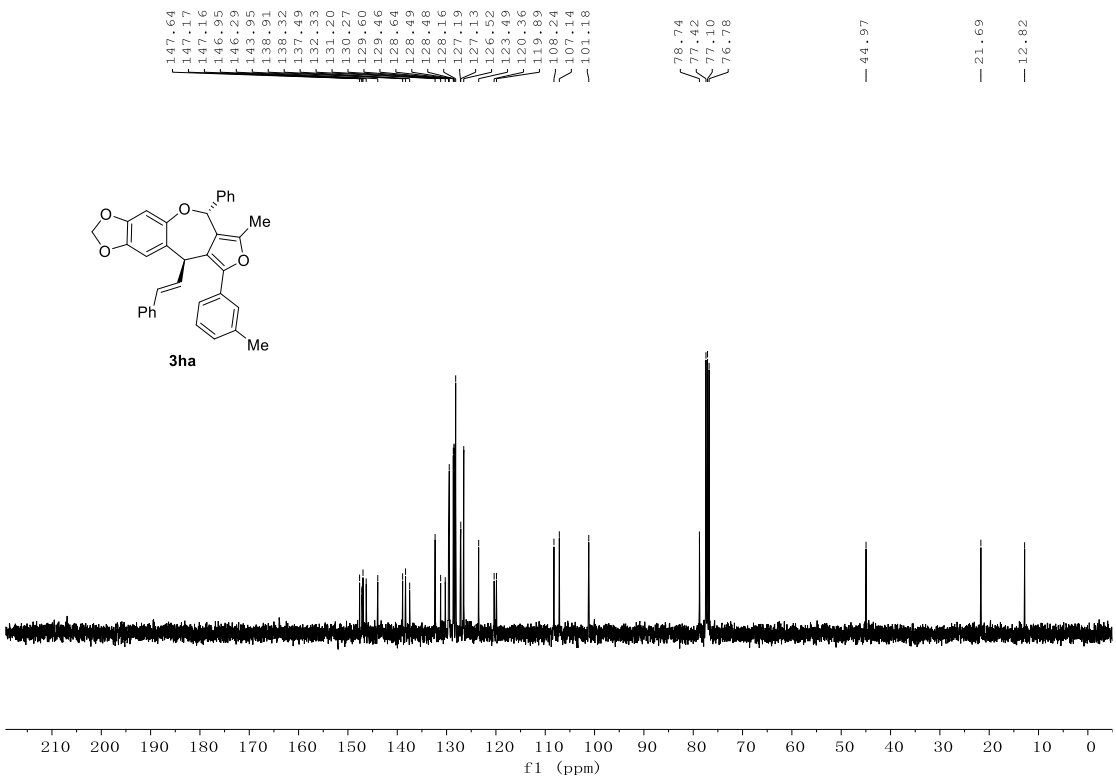
7.263
7.245
7.225
7.188
7.169
7.149
7.129
7.101
7.086
6.875
6.859
6.835
6.820
6.645
6.519
6.479
6.343
5.764
5.679
4.662
4.647
2.412
1.803
0.000
Ph
Me
Ph
Me
3ha
0.98
1.17
2.01
1.00
5.15
1.97
1.98
0.96
0.98
1.03
1.01
2.05
1.02
0.99
2.98
3.00
f1 (ppm)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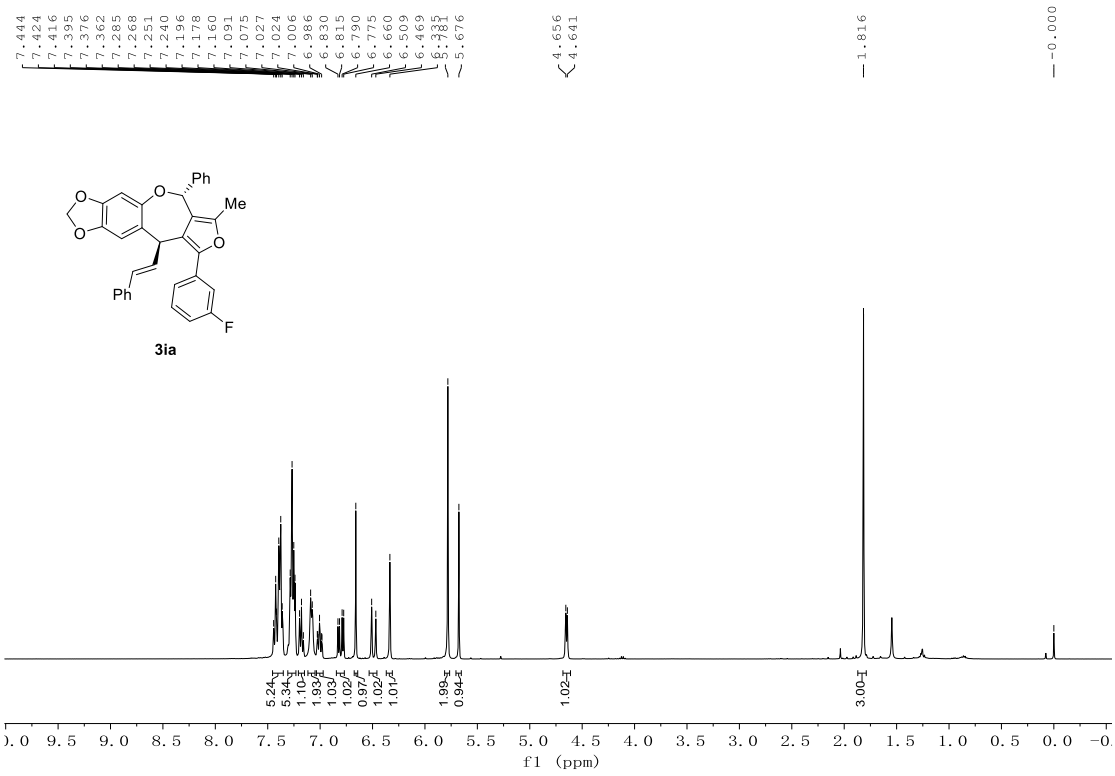
143.95
138.91
138.32
137.49
132.33
131.20
130.27
129.60
129.46
128.64
128.49
128.48
128.16
127.19
127.13
126.52
123.49
120.36
119.89
108.24
107.14
101.18
78.74
77.42
77.10
76.78
44.97
21.69
12.82
Ph
Me
Ph
Me
3ha
f1 (ppm)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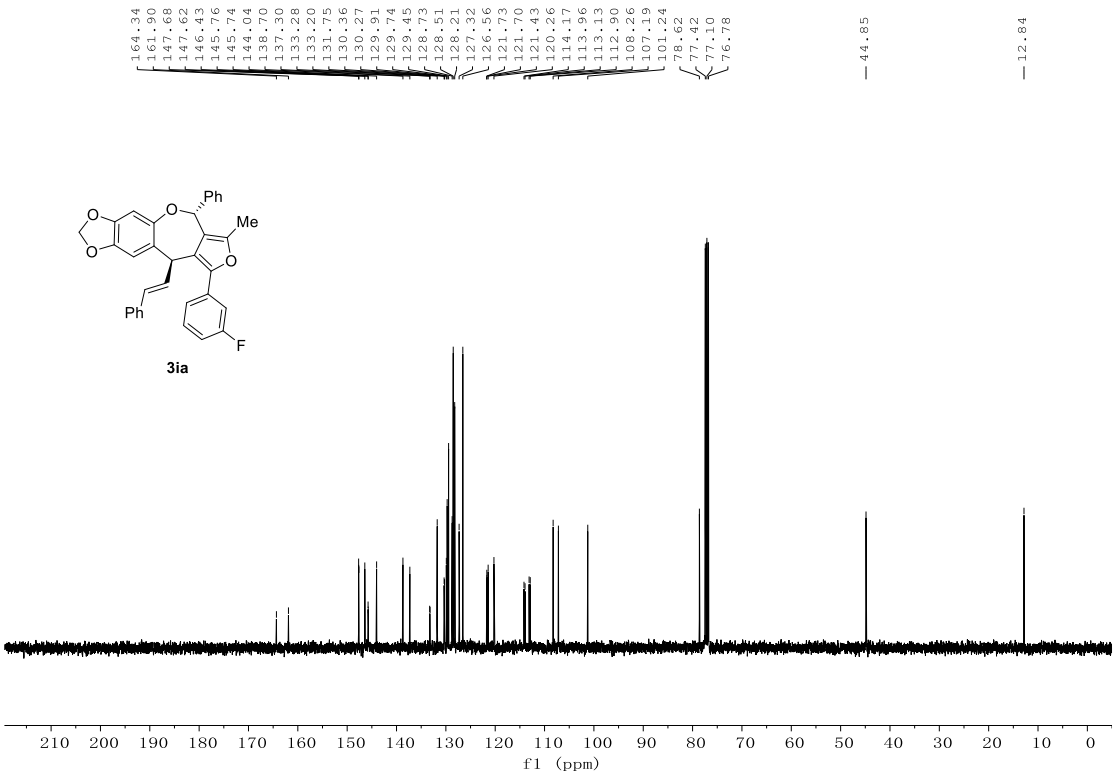
7.285
7.268
7.251
7.240
7.196
7.178
7.160
7.091
7.075
7.027
7.024
7.006
6.386
6.830
6.815
6.790
6.775
6.660
6.509
6.469
6.335
5.781
5.676
4.656
4.641
1.816
-0.000
Ph
Me
Ph
F
3ia
5.24
5.34
1.10
1.93
1.03
1.02
0.97
1.02
1.01
1.99
0.94
1.02
3.00
f1 (ppm)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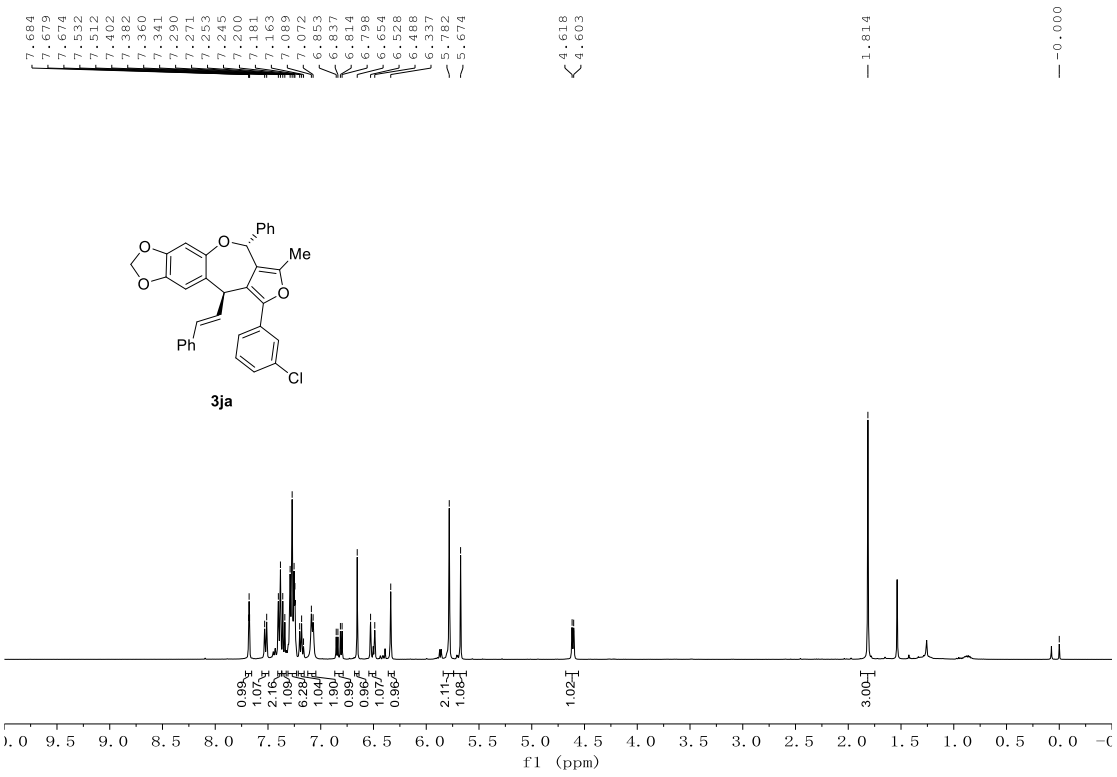
161.90
147.68
147.62
146.43
145.76
145.74
144.04
138.70
137.30
133.28
133.20
131.75
130.36
130.27
129.91
129.74
129.45
128.73
128.51
128.21
127.32
126.56
121.73
121.70
121.43
120.26
114.17
113.96
113.13
112.90
108.26
107.19
101.24
78.62
77.42
77.10
76.78
44.85
12.84
Ph
Me
Ph
F
3ia
f1 (ppm)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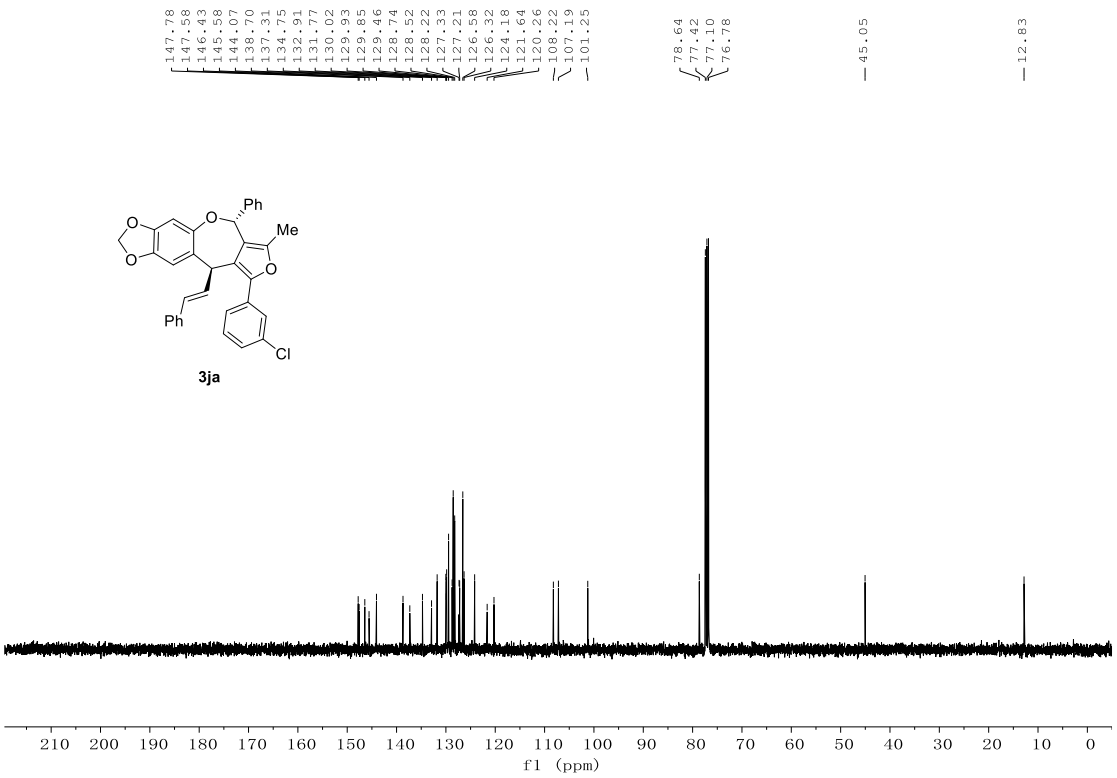
7.360
7.341
7.290
7.271
7.253
7.245
7.200
7.181
7.163
7.089
7.072
6.853
6.837
6.814
6.798
6.654
6.528
6.488
6.337
5.782
5.674
4.618
4.603
1.814
-0.000
Ph
Me
O
O
O
Ph
Cl
3ja
0.99
1.07
2.16
1.09
6.28
1.04
1.90
0.99
0.96
1.07
0.96
2.11
1.08
1.02
3.00
f1 (ppm)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144.07
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137.31
134.75
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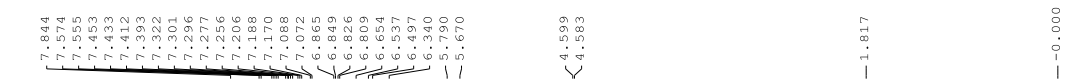
131.77
130.02
129.93
129.85
129.46
128.74
128.52
128.22
127.33
127.21
126.58
126.32
124.18
121.64
120.26
108.22
107.19
101.25
78.64
77.42
77.10
76.78
45.05
12.83
Ph
Me
O
O
O
Ph
Cl
3ja
f1 (ppm)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7.322
7.301
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7.277
7.256
7.206
7.188
7.170
7.088
7.072
6.865
6.849
6.826
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6.497
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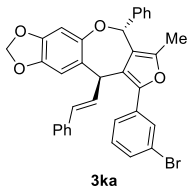
4.599
4.583
1.817
-0.000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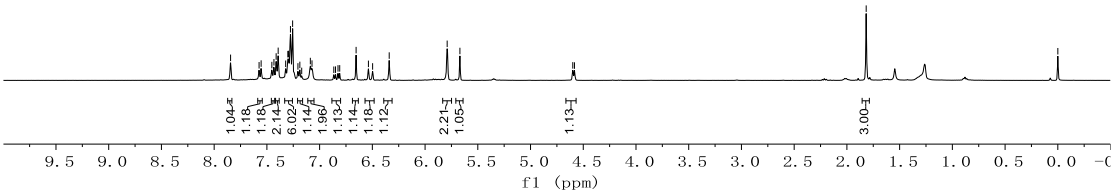
O
O
O
Me
O
Ph
Br

3ka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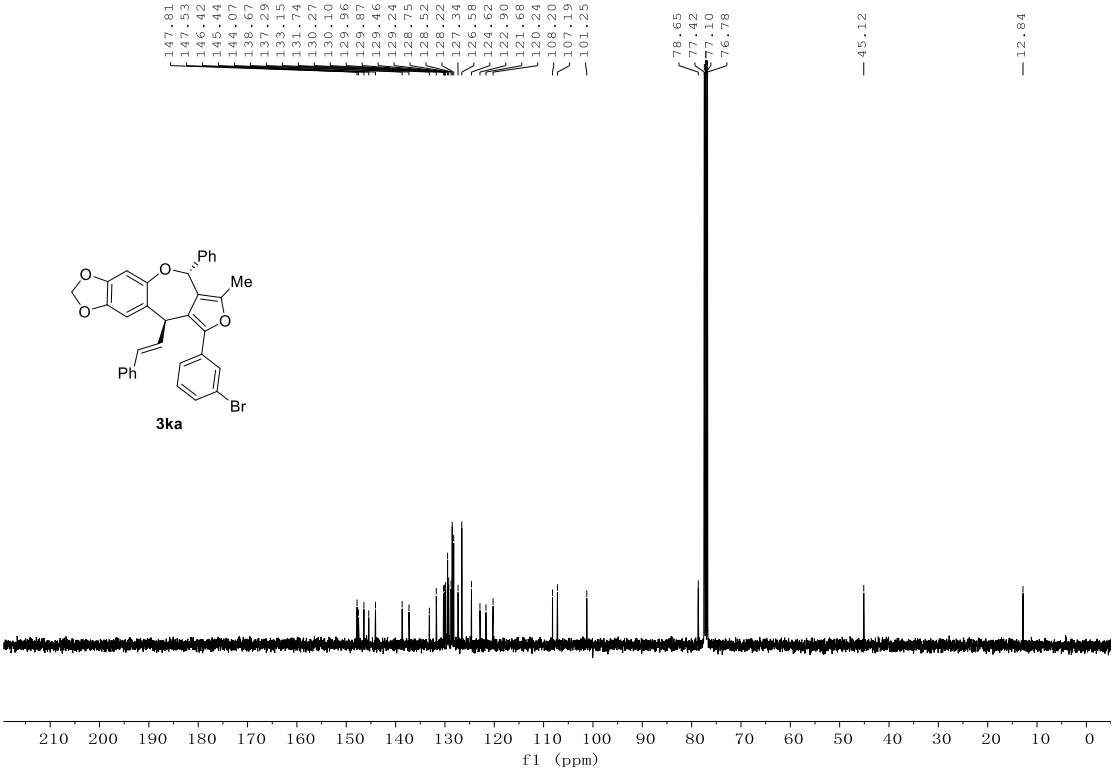
1.18
1.18
2.14
6.02
1.14
1.96
1.13
1.14
1.18
1.12
2.21
1.05
1.13
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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145.44
144.07
138.67
137.29
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131.74
130.27
130.10
129.96
129.87
129.46
129.24
128.75
128.52
128.22
127.34
126.58
124.62
122.90
121.68
120.24
108.20
107.19
101.25
78.65
77.42
77.10
76.78
45.12
12.84
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Ph
O
O
O
Me
O
Ph
Br

3ka


7.535
7.372
7.353
7.333
7.314
7.290
7.286
7.272
7.262
7.247
7.244
7.231
7.224
7.214
7.194
7.174
7.171
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7.117
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6.296
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5.739
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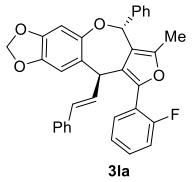
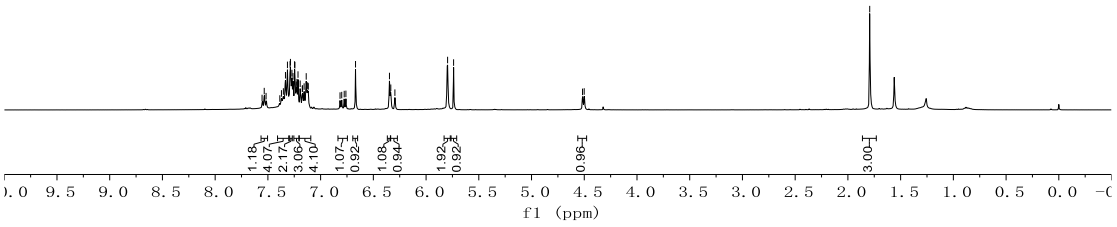
4.501
1.793


Ph
Me
O
O
O
O
Ph
F

3la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3.06
4.10
1.07
0.92
1.08
0.94
1.92
0.92
0.96
3.00
f1 (ppm)


160.82
158.34
148.16
147.70
146.32
143.92
141.70
138.90
137.49
132.50
130.80
130.77
129.98
129.92
129.84
129.35
129.27
128.66
128.44
128.23
127.13
126.45
124.27
124.23
123.07
119.38
119.32
119.18
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116.22
108.22
107.04
101.21
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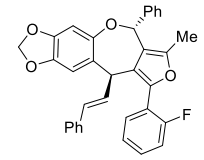
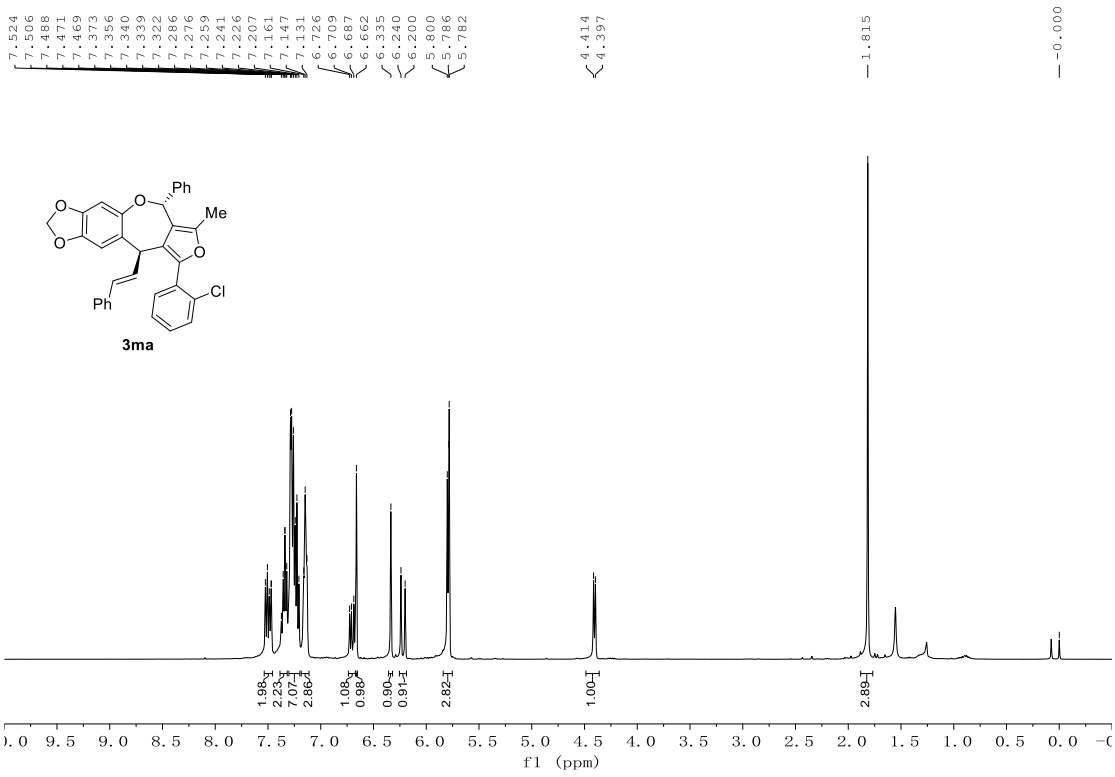
77.42
77.10
76.78
44.43
12.87


Ph
Me
O
O
O
O
Ph
F

3la

f1 (ppm)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7.322
7.286
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7.259
7.241
7.226
7.207
7.161
7.147
7.131
6.726
6.709
6.687
6.662
6.335
6.240
6.200
5.800
5.786
5.782
4.414
4.397
1.815
-0.000
Ph
Me
O
O
O
O
Ph
Cl
3ma
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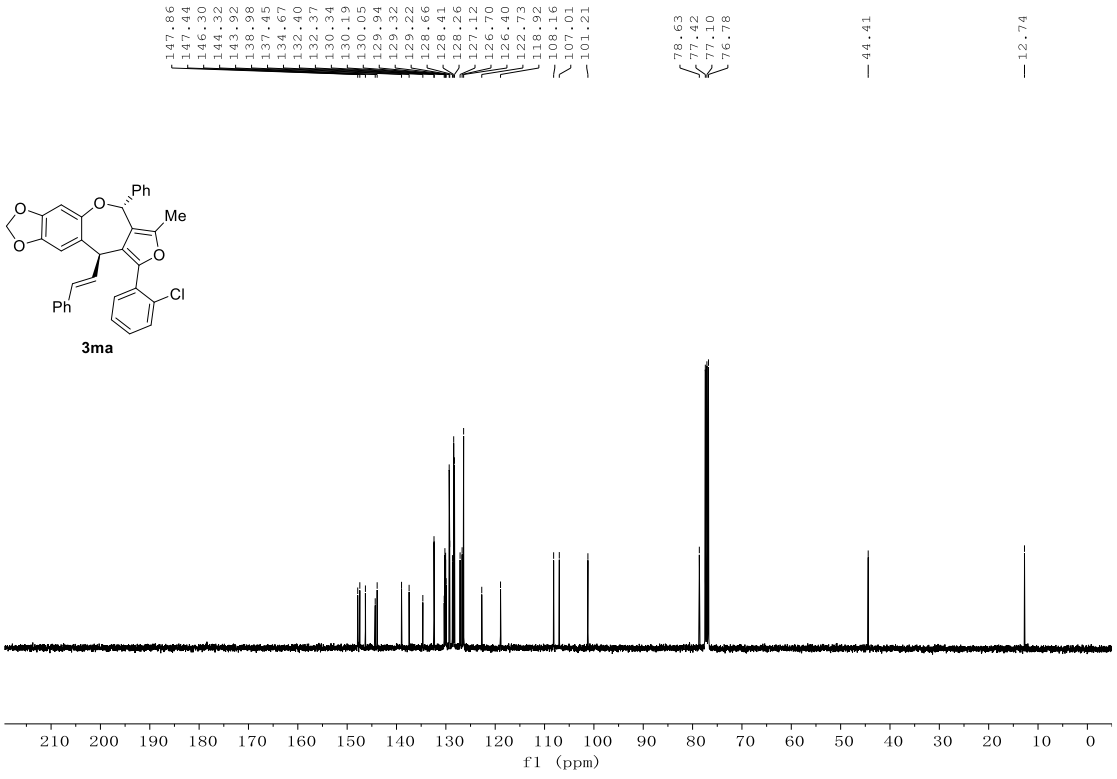
7.07
2.86
1.08
0.98
0.90
0.91
2.82
1.00
2.89
f1 (ppm)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144.32
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138.98
137.45
134.67
132.40
132.37
130.34
130.19
130.05
129.94
129.32
129.22
128.66
128.41
128.26
127.12
126.70
126.40
122.73
118.92
108.16
107.01
101.21
78.63
77.42
77.10
76.78
44.41
12.74
Ph
Me
O
O
O
O
Ph
Cl
3ma
f1 (ppm)


8.112
7.916
7.894
7.877
7.873
7.858
7.843
7.839
7.819
7.814
7.797
7.793
7.518
7.505
7.501
7.495
7.488
7.481
7.476
7.472
7.440
7.422
7.305
7.286
7.283
7.267
7.250
7.233
7.209
7.191
7.173
7.129
7.114
6.950
6.934
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6.617
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6.380
5.767
5.690
4.761
4.746
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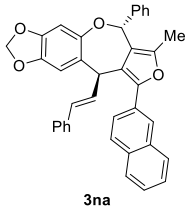
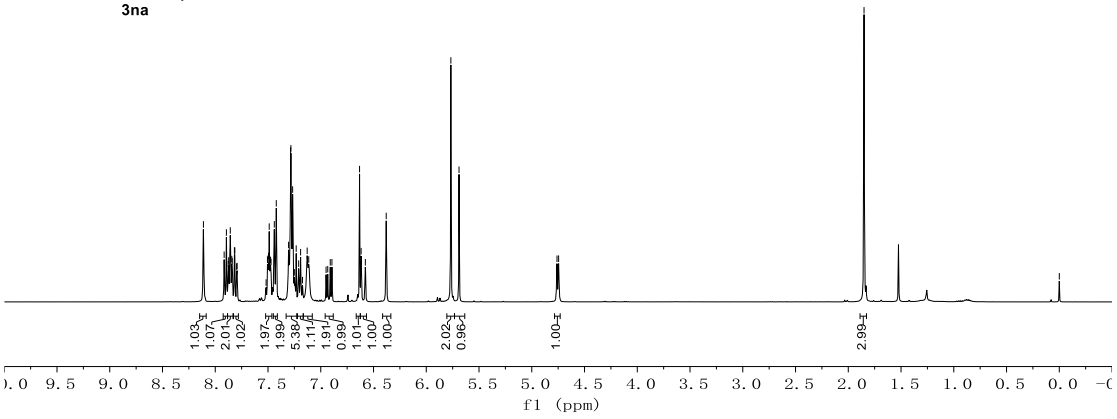
0.000


Ph
O
Me
O
O
O
Ph

3na


1.03
1.07
2.01
1.02
1.97
1.99
5.38
1.11
1.91
0.99
1.01
1.00
1.00
2.02
0.96
1.00
2.99
f1 (ppm)


147.59
147.44
147.13
146.33
143.99
138.83
137.45
133.50
132.56
132.27
130.27
129.79
129.50
128.69
128.53
128.41
128.31
128.20
127.81
127.28
126.57
126.52
126.49
126.12
125.08
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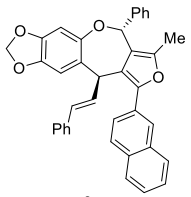
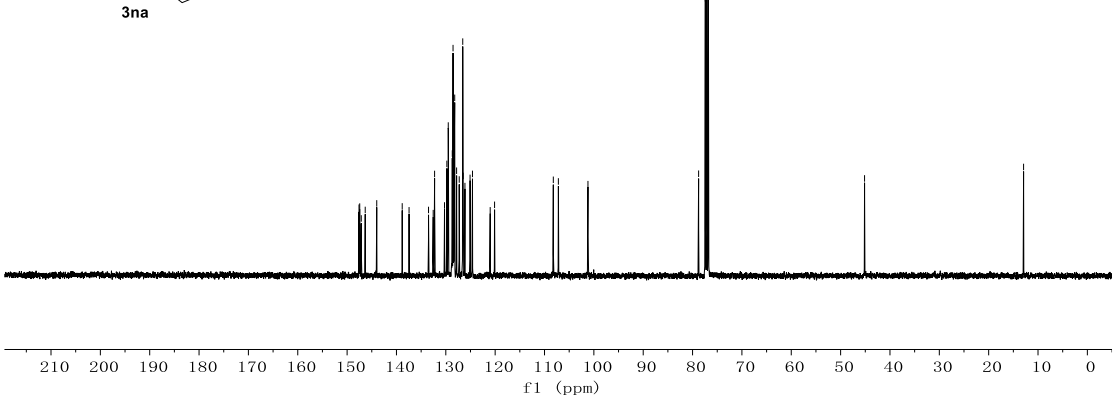
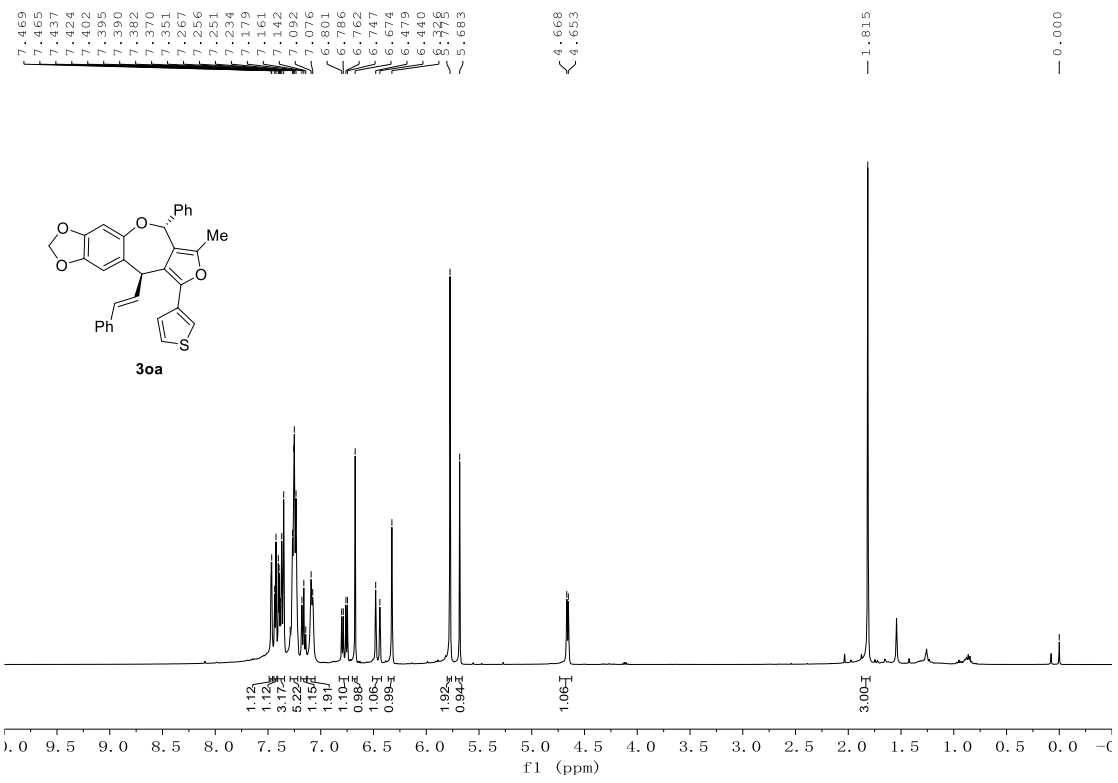
45.15
12.92


Ph
O
Me
O
O
O
Ph

3na


f1 (ppm)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7.382
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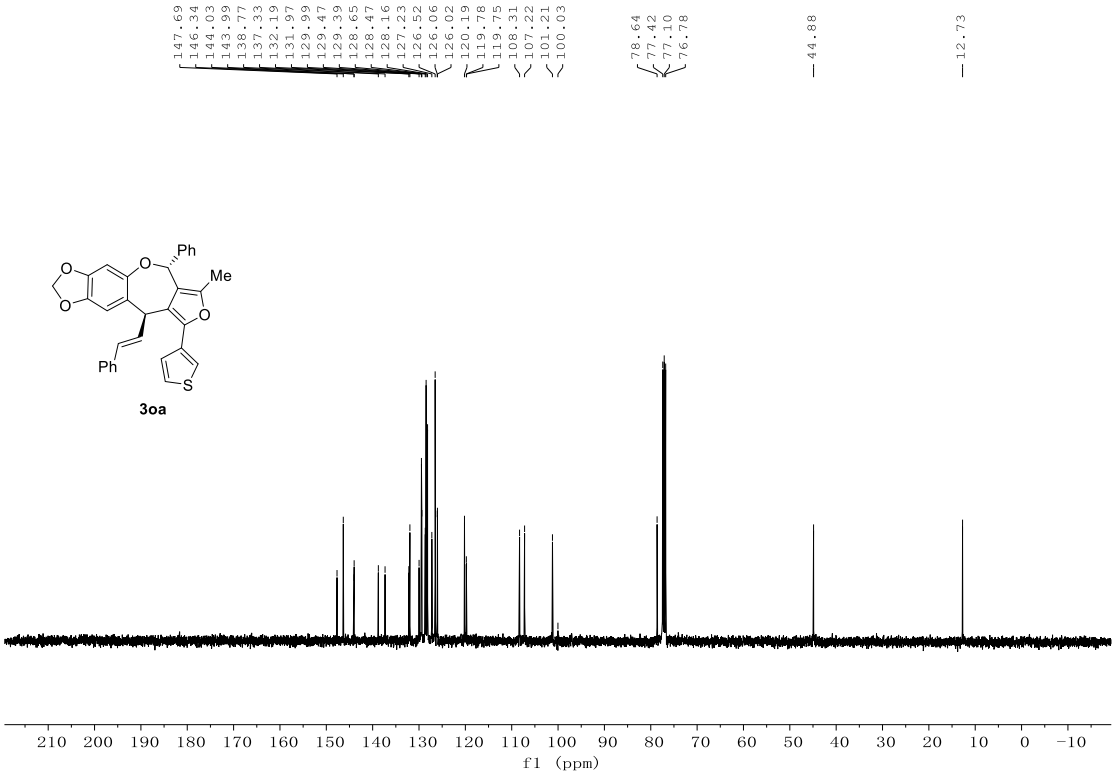
7.351
7.267
7.256
7.251
7.234
7.179
7.161
7.142
7.092
7.076
6.801
6.786
6.762
6.747
6.674
6.479
6.440
5.746
5.683
4.668
4.653
1.815
0.000
Ph
Me
O
O
O
Ph
S
3oa
1.12
1.12
3.17
5.22
1.15
1.91
1.10
0.98
1.06
0.99
1.92
0.94
1.06
3.00
f1 (ppm)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132.19
131.97
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129.47
129.39
128.65
128.47
128.16
127.23
126.52
126.06
126.02
120.19
119.78
119.75
108.31
107.22
101.21
100.03
78.64
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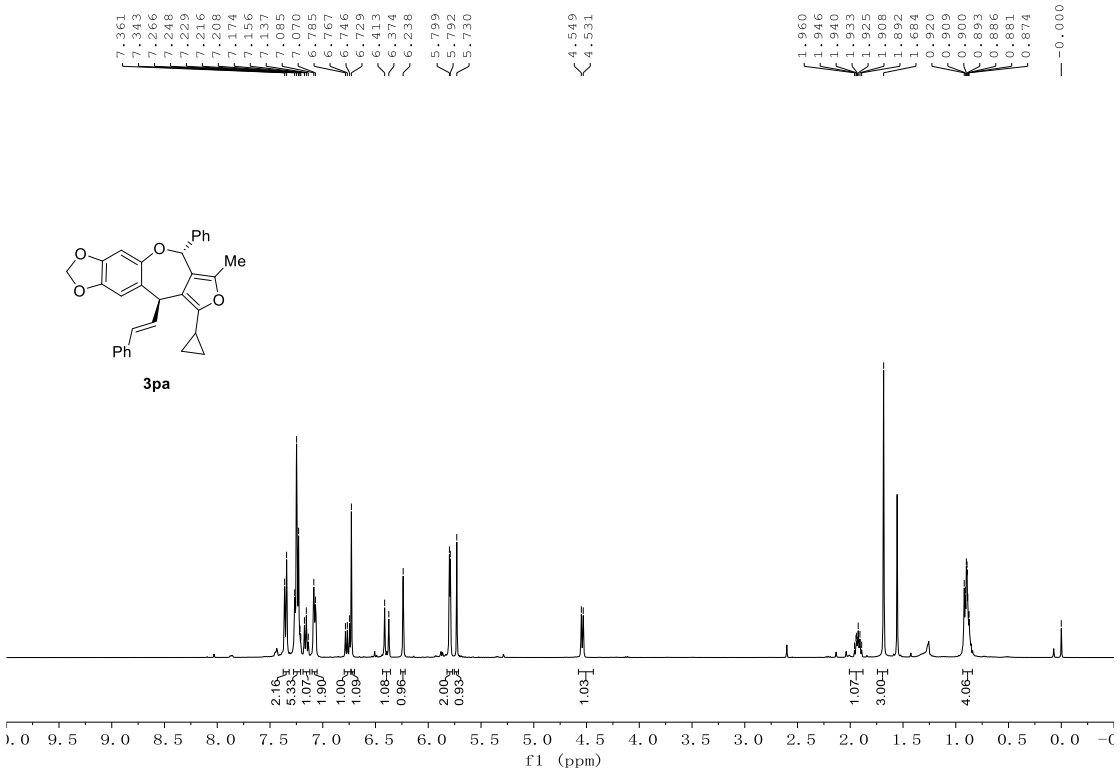
76.78
44.88
12.73
Ph
Me
O
O
O
Ph
S
3oa
f1 (ppm)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7.137
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7.070
6.785
6.767
6.746
6.729
6.413
6.374
6.238
5.799
5.792
5.730
4.549
4.531
1.960
1.946
1.940
1.933
1.925
1.908
1.892
1.684
0.920
0.909
0.900
0.893
0.886
0.881
0.874
0.000
Ph
Me
O
O
O
Ph
3pa
2.16
5.33
1.07
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1.08
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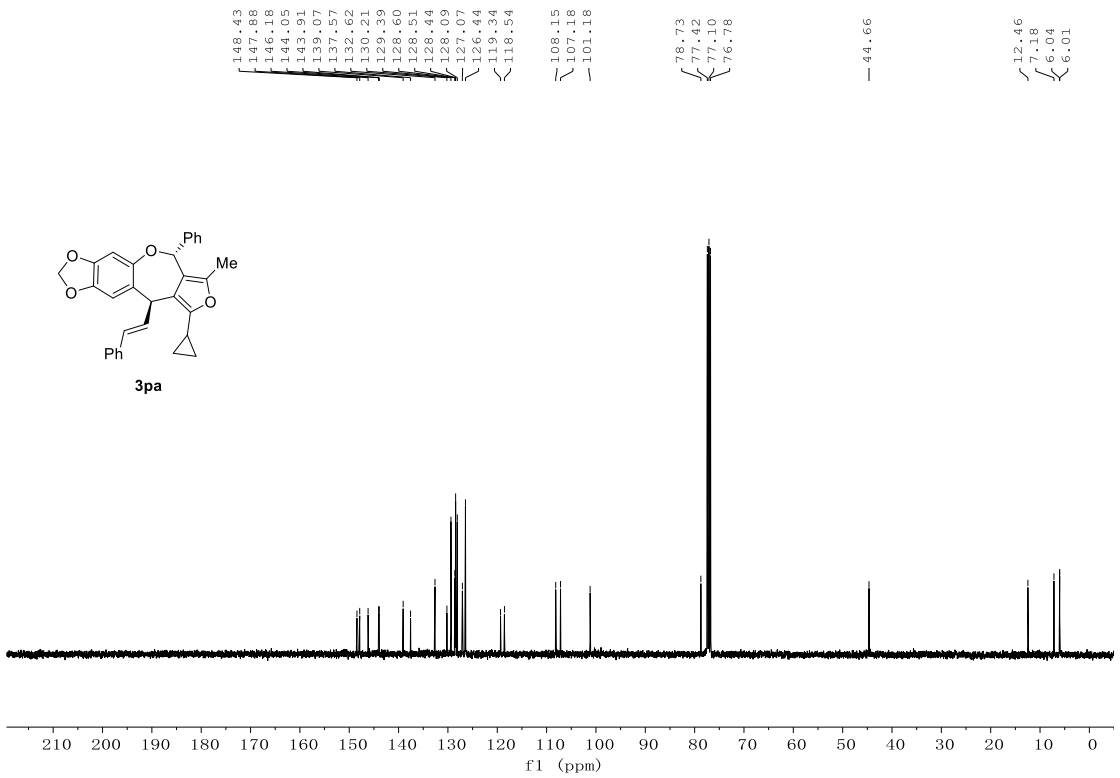
2.00
0.93
1.03
1.07
3.00
4.06
f1 (ppm)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128.44
128.09
127.07
126.44
119.34
118.54
108.15
107.18
101.18
78.73
77.42
77.10
76.78
44.66
12.46
7.18
6.04
6.01
Ph
Me
O
O
O
Ph
3pa
f1 (ppm)


7.660
7.640
7.449
7.430
7.411
7.388
7.369
7.324
7.305
7.275
7.256
7.237
7.224
7.182
7.164
7.055
7.036
6.978
6.960
6.848
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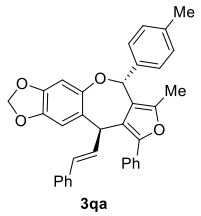
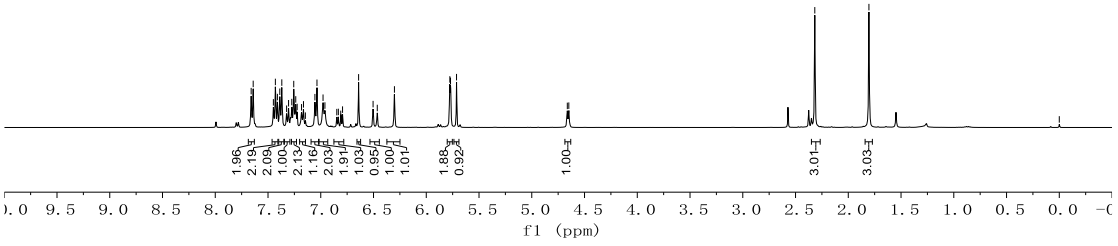
1.804
0.000


Me
O
O
O
Me
O
Ph
Ph

3qa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1.91
1.03
0.95
1.00
1.01
1.88
0.92
1.00
3.01
3.03
f1 (ppm)


147.68
147.11
146.90
146.26
143.89
138.30
137.45
135.93
132.23
131.31
130.28
129.49
129.38
128.85
128.74
128.46
127.25
127.18
126.53
126.29
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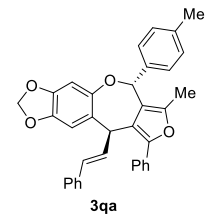
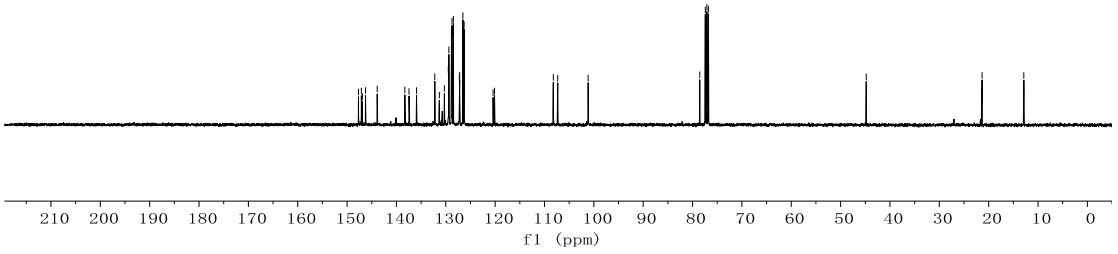
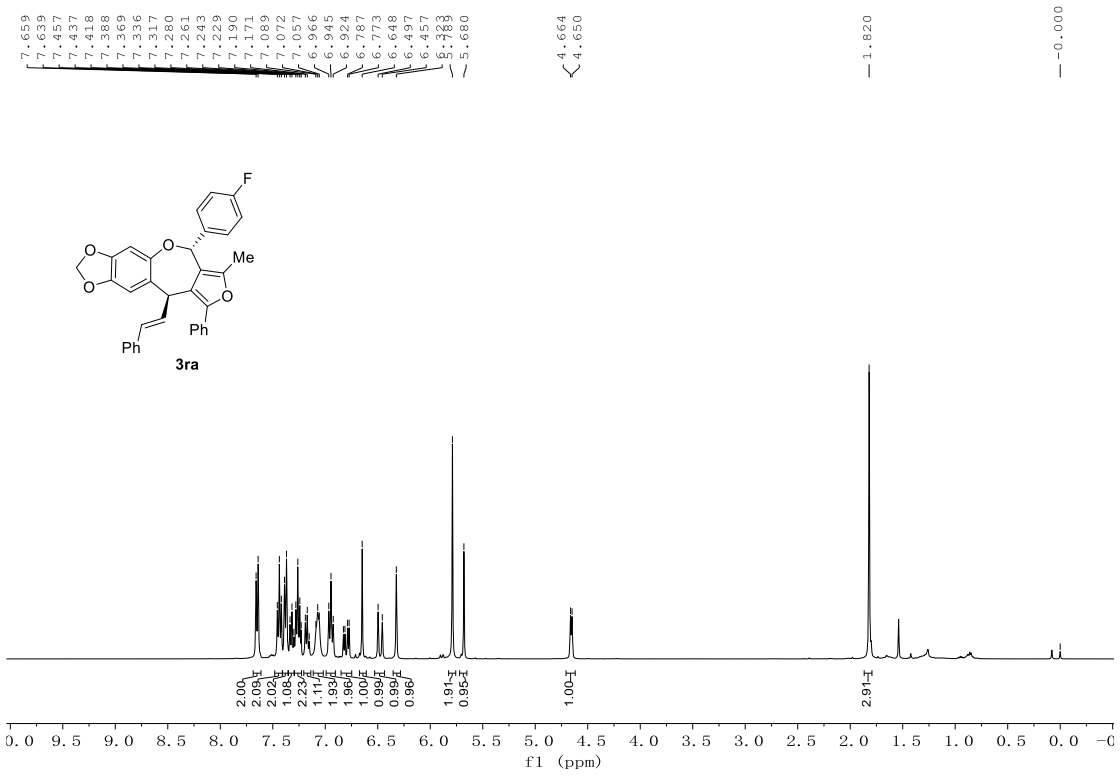
77.42
77.10
76.78
44.81
21.33
12.88


Me
O
O
O
Me
O
Ph
Ph

3qa


f1 (ppm)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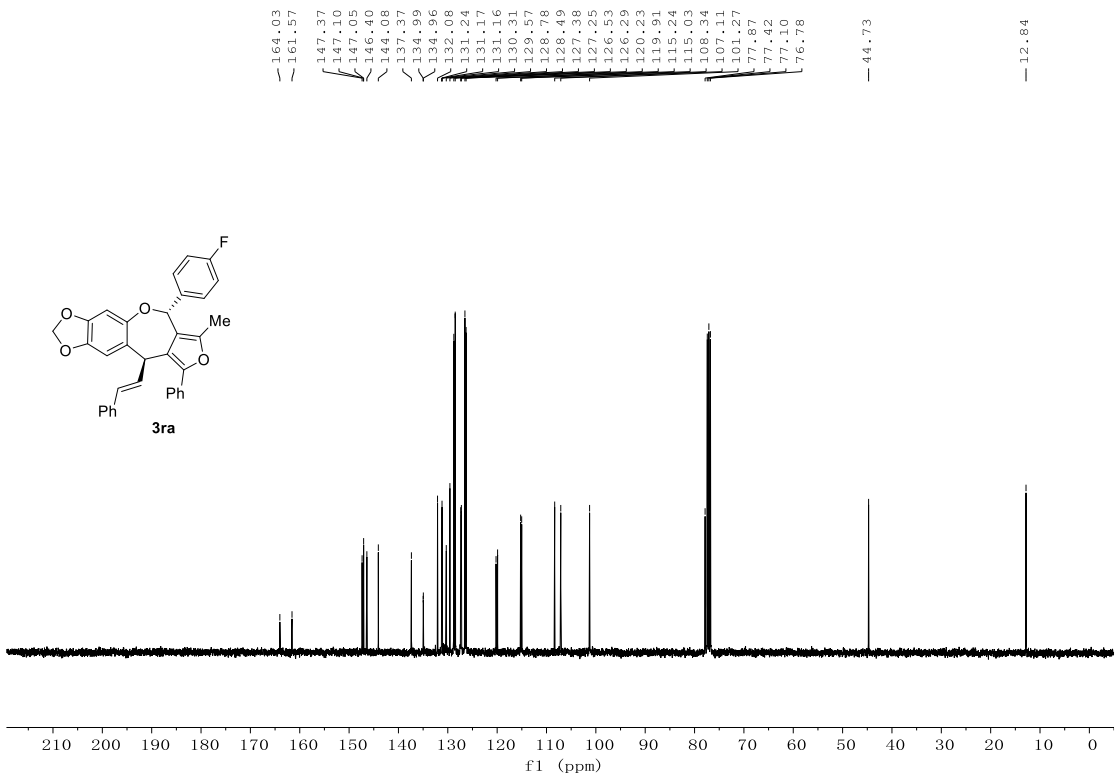
7.243
7.229
7.190
7.171
7.089
7.072
7.057
6.966
6.945
6.924
6.787
6.773
6.648
6.497
6.457
5.783
5.680
4.664
4.650
1.820
-0.000
F
O
O
O
Me
O
Ph
Ph
3ra
2.00
2.09
2.02
1.08
2.23
1.11
1.93
1.96
1.00
0.99
0.99
0.98
1.91
0.95
1.00
2.91
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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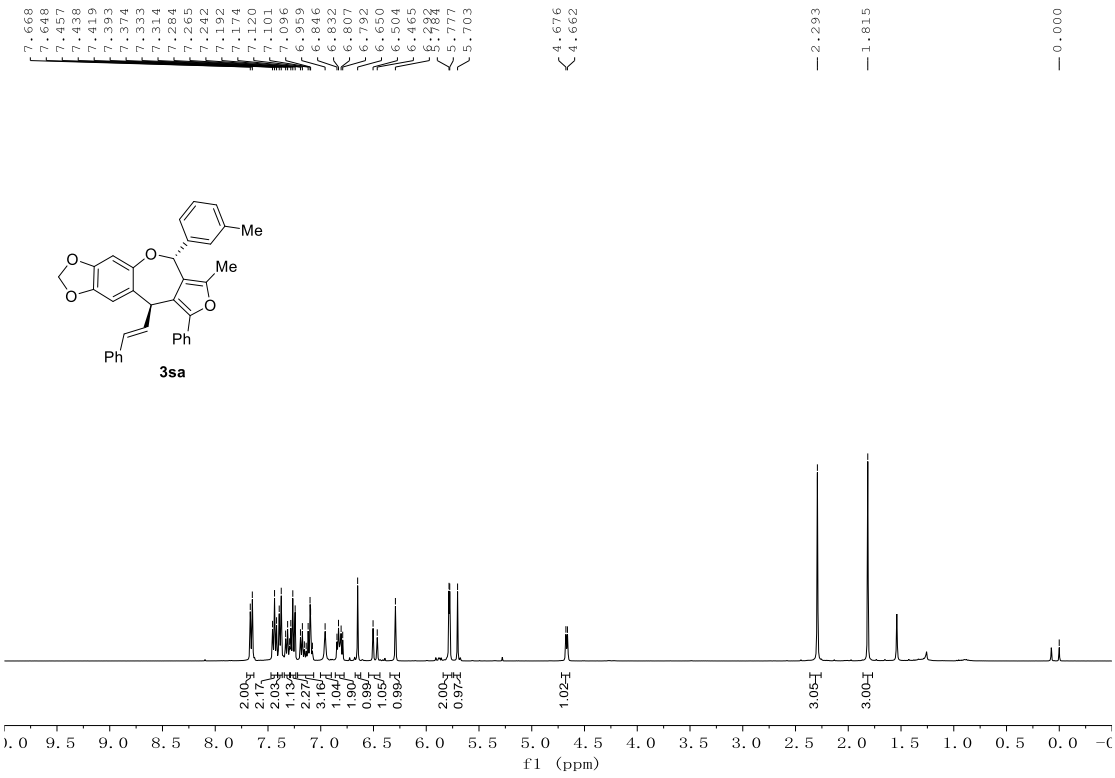
147.05
146.40
144.08
137.37
134.99
134.96
132.08
131.24
131.17
131.16
130.31
129.57
128.78
128.49
127.38
127.25
126.53
126.29
120.23
119.91
115.24
115.03
108.34
107.11
101.27
77.87
77.42
77.10
76.78
44.73
12.84
F
O
O
O
Me
O
Ph
Ph
3ra
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.265
7.242
7.192
7.174
7.120
7.101
7.096
6.959
6.846
6.832
6.807
6.792
6.650
6.504
6.465
5.777
5.703
4.676
4.662
2.293
1.815
0.000
Me
Me
Ph
Ph
3sa
2.00
2.17
2.03
1.13
2.27
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1.04
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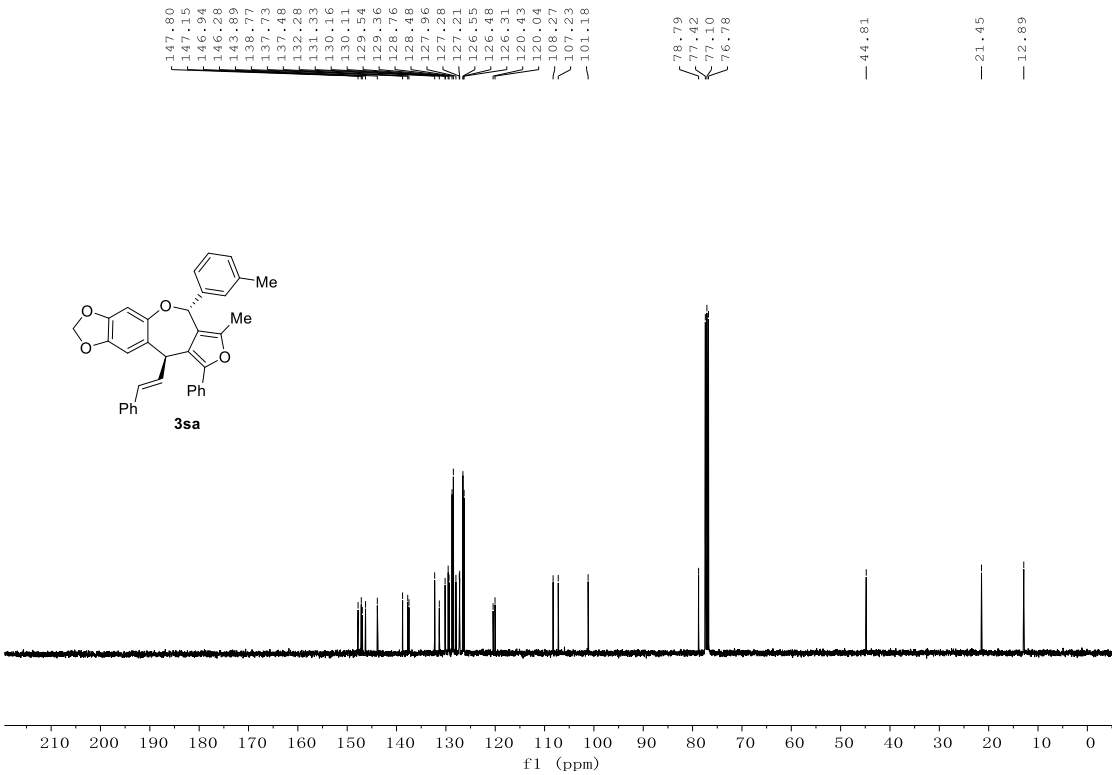
0.99
1.05
0.99
2.00
0.97
1.02
3.05
3.00
f1 (ppm)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131.33
130.16
130.11
129.54
129.36
128.76
128.48
127.96
127.28
127.21
126.55
126.48
126.31
120.43
120.04
108.27
107.23
101.18
78.79
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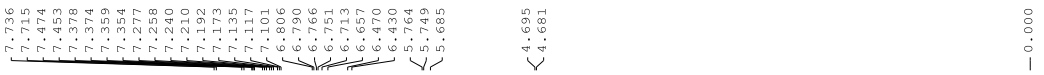
77.10
76.78
44.81
21.45
12.89
Me
Me
Ph
Ph
3sa
f1 (ppm)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7.192
7.173
7.135
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7.101
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6.790
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6.657
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6.430
5.764
5.749
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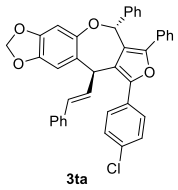
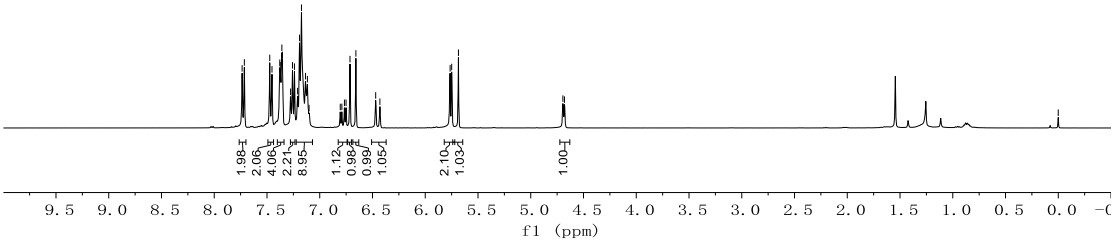
4.681
0.000


Ph
Ph
Ph
Cl

3ta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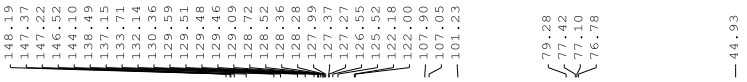
2.06
4.06
2.21
8.95
1.12
0.98
0.99
1.05
2.10
1.03
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.51
129.48
129.46
129.09
128.72
128.52
128.36
128.28
127.99
127.37
127.27
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122.00
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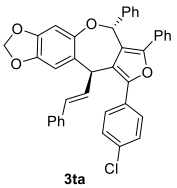
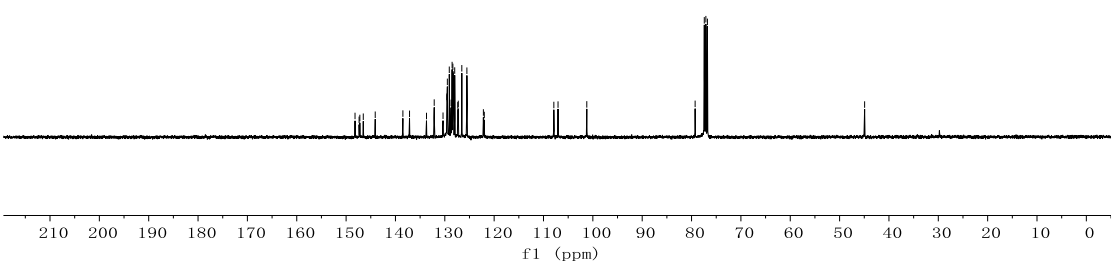
107.05
101.23
79.28
77.42
77.10
76.78
44.93


Ph
Ph
Ph
Cl

3ta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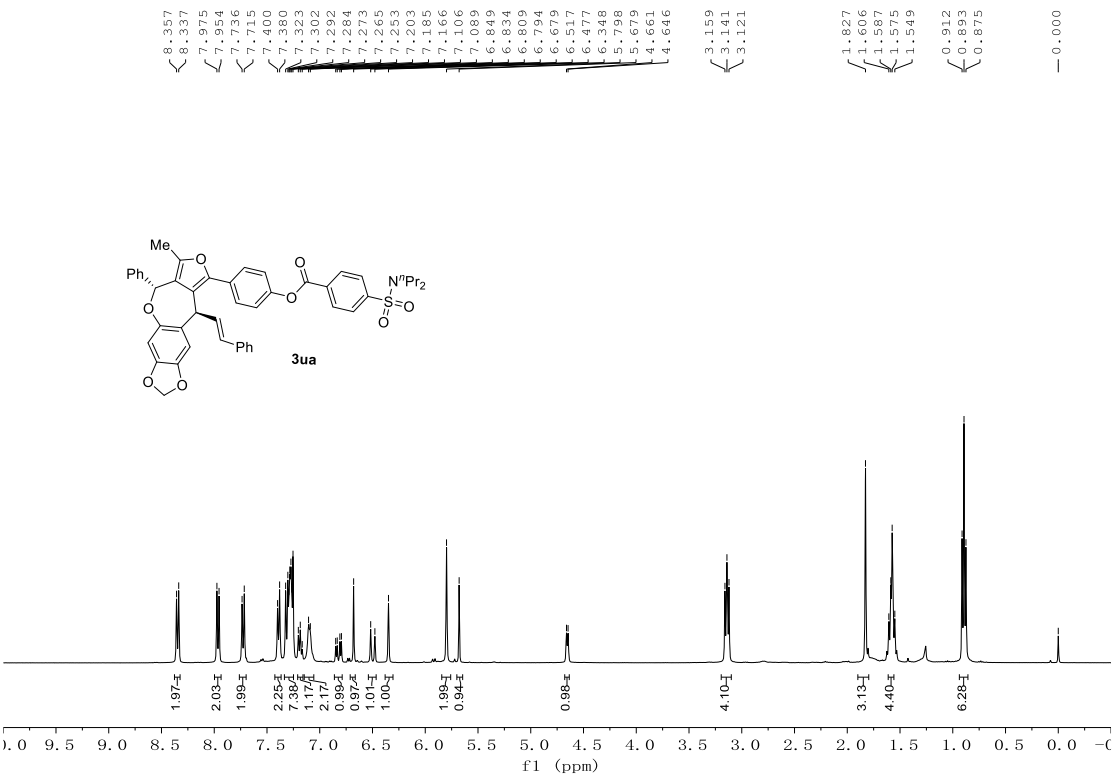
f1 (ppm)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7.302
7.292
7.284
7.273
7.265
7.253
7.203
7.185
7.166
7.106
7.089
6.849
6.834
6.809
6.794
6.679
6.517
6.477
6.348
5.798
5.679
4.661
4.646
3.159
3.141
3.121
1.827
1.606
1.587
1.575
1.549
0.912
0.893
0.875
0.000
Me
Ph
O
O
O
O
O
O
O
N^{n}Pr$_2$
S
O
O
Ph
3ua
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2.03
1.99
2.25
7.38
1.17
2.17
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0.97
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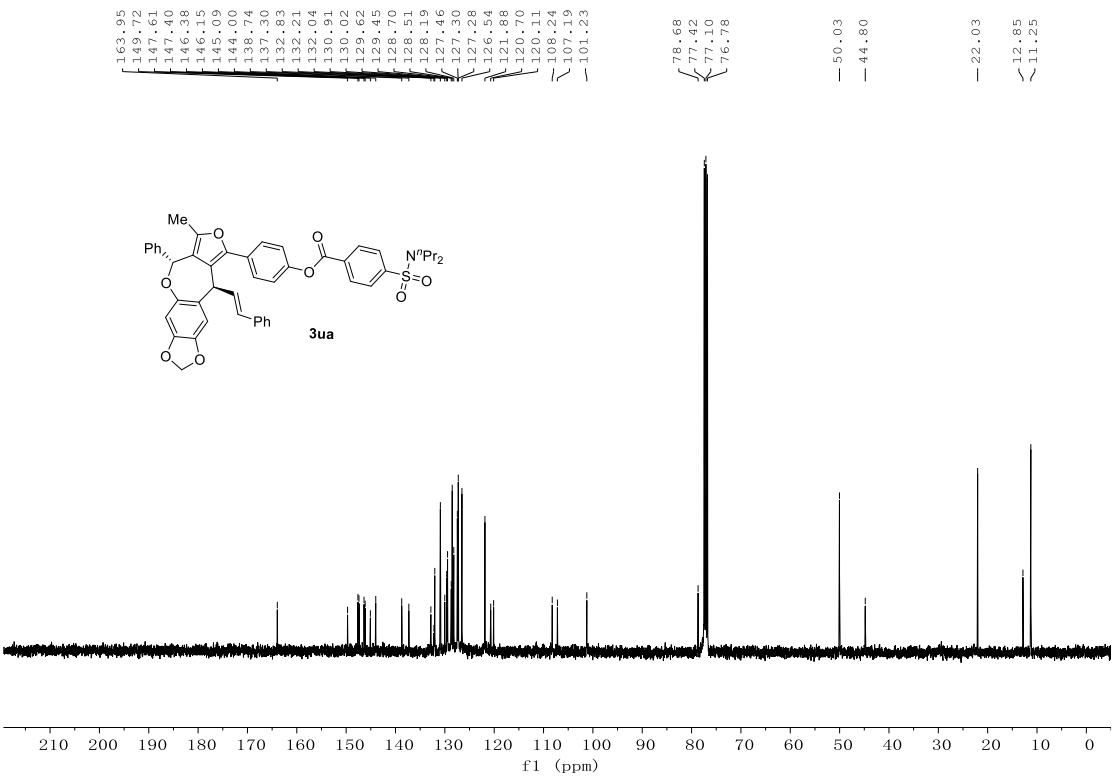
1.99
0.94
0.98
4.10
3.13
4.40
6.28
f1 (ppm)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132.21
132.04
130.91
130.02
129.62
129.45
128.70
128.51
128.19
127.46
127.30
127.28
126.54
121.88
120.70
120.11
108.24
107.19
101.23
78.68
77.42
77.10
76.78
50.03
44.80
22.03
12.85
11.25
Me
Ph
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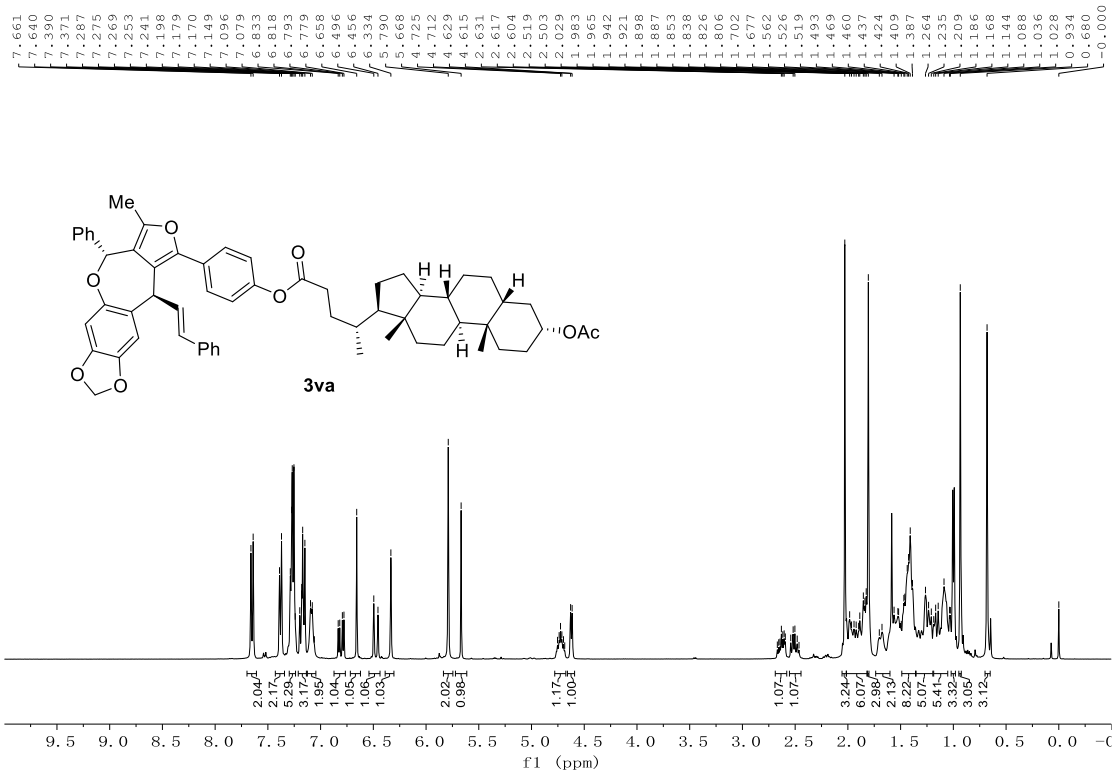
O
O
O
O
O
N^{n}Pr$_2$
S
O
O
Ph
3ua
f1 (ppm)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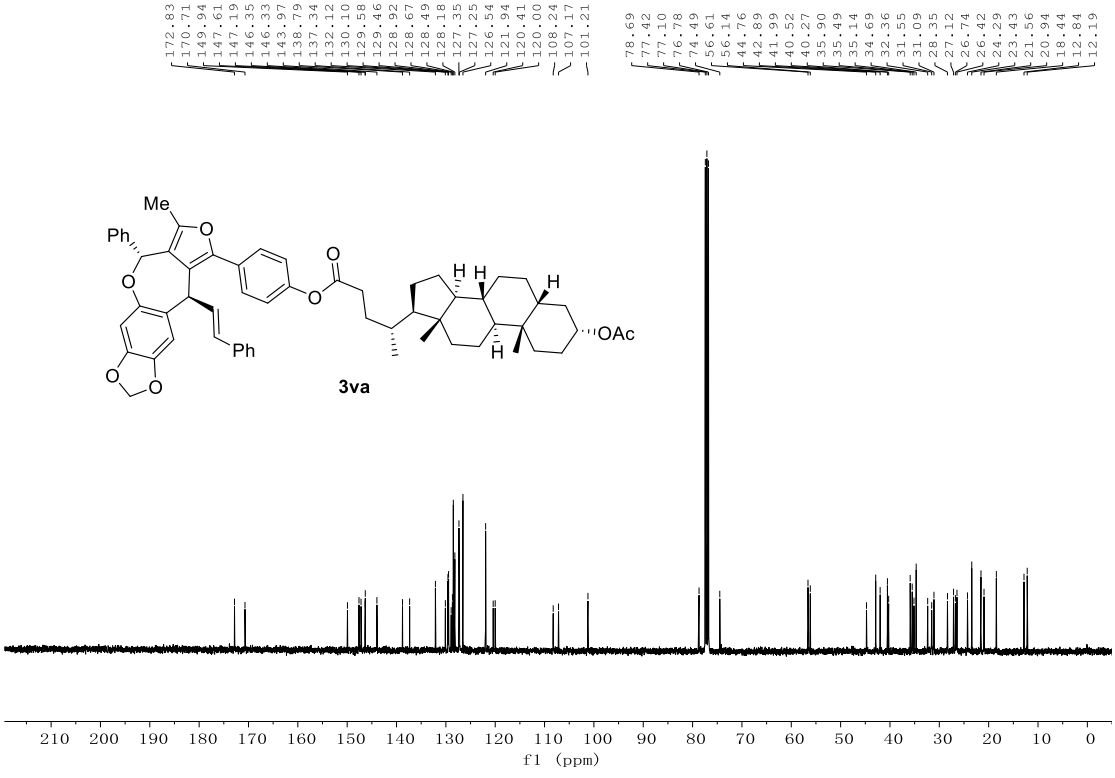
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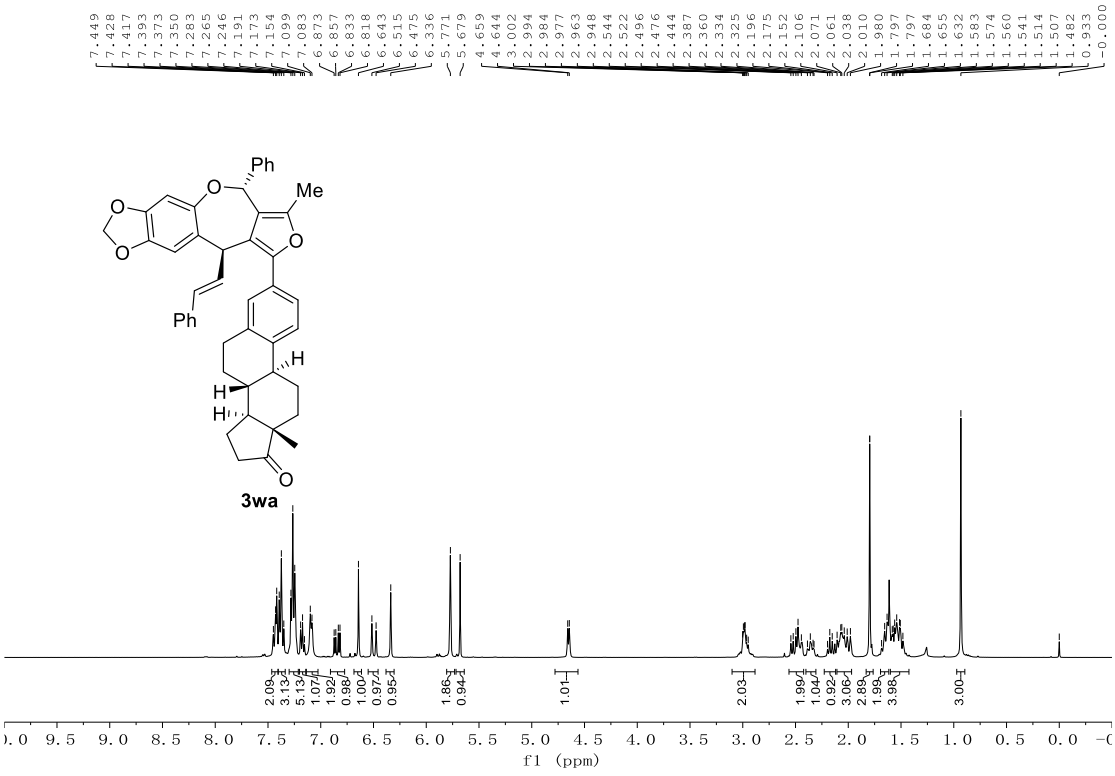
f1 (ppm)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7.265
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7.191
7.173
7.154
7.099
7.083
6.873
6.857
6.833
6.818
6.643
6.515
6.475
6.336
5.771
5.679
4.659
4.644
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2.984
2.977
2.963
2.948
2.544
2.522
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2.476
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2.387
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2.325
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2.061
2.038
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1.574
1.560
1.541
1.514
1.507
1.482
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Ph
Me
O
O
O
Ph
H
H
H
O
3wa
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3.13
5.13
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0.98
1.00
0.97
0.95
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1.99
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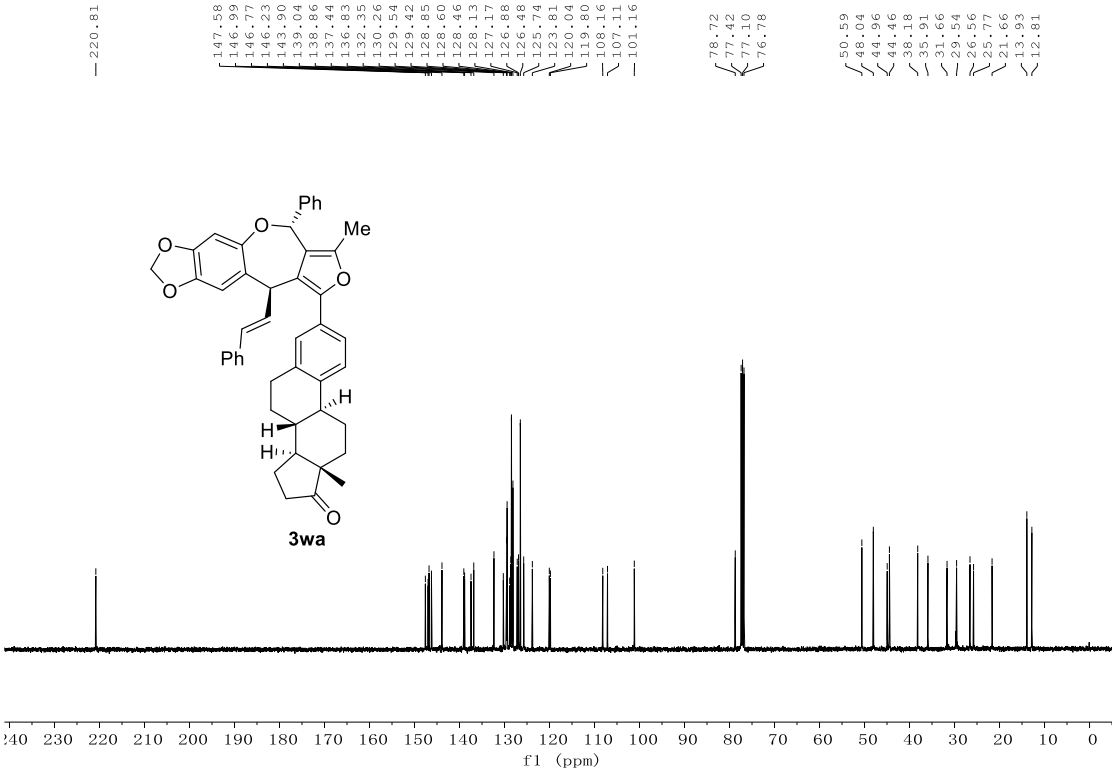
3.00
f1 (ppm)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136.83
132.35
130.26
129.54
129.42
128.85
128.60
128.46
128.13
127.17
126.88
126.48
125.74
123.81
120.04
119.80
108.16
107.11
101.16
78.72
77.42
77.10
76.78
50.59
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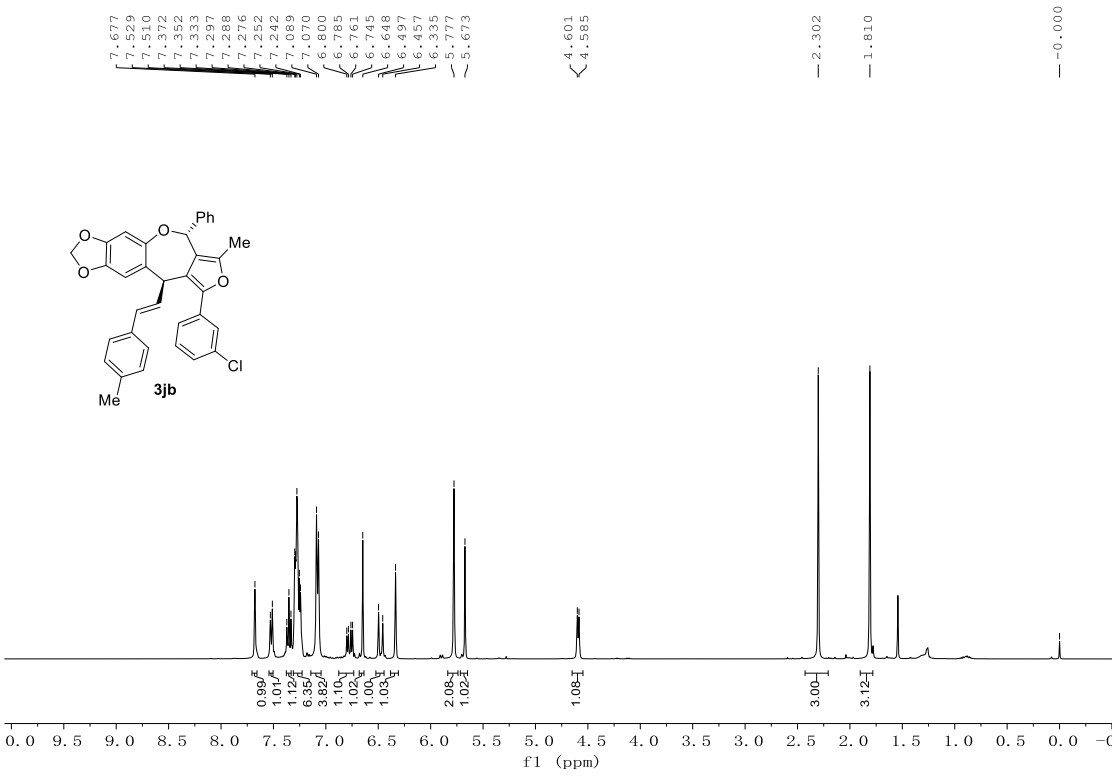
44.96
44.46
38.18
35.91
31.66
29.54
26.56
25.77
21.66
13.93
12.81
Ph
Me
O
O
O
Ph
H
H
H
O
3wa
f1 (ppm)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7.242
7.089
7.070
6.800
6.785
6.761
6.745
6.648
6.497
6.457
6.335
5.777
5.673
4.601
4.585
2.302
1.810
-0.000
Ph
Me
Cl
Me
3jb
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1.01
1.12
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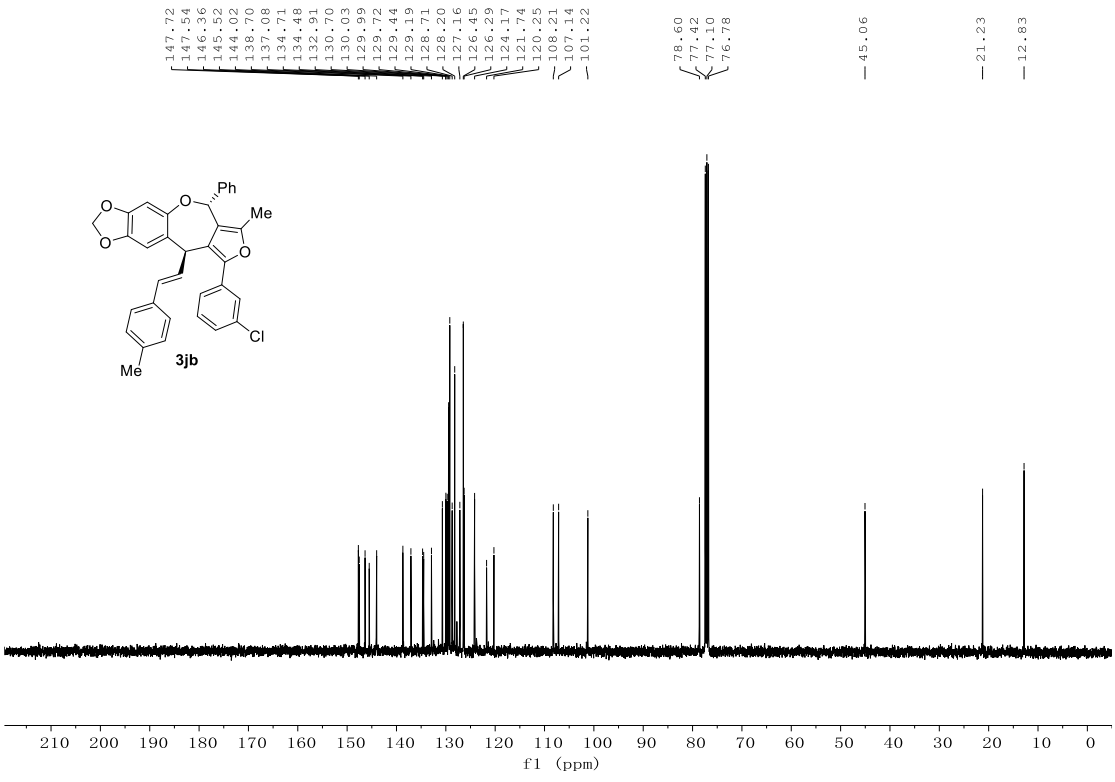
1.08
3.00
3.12
f1 (ppm)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146.36
145.52
144.02
138.70
137.08
134.71
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132.91
130.70
130.03
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129.19
128.71
128.20
127.16
126.45
126.29
124.17
121.74
120.25
108.21
107.14
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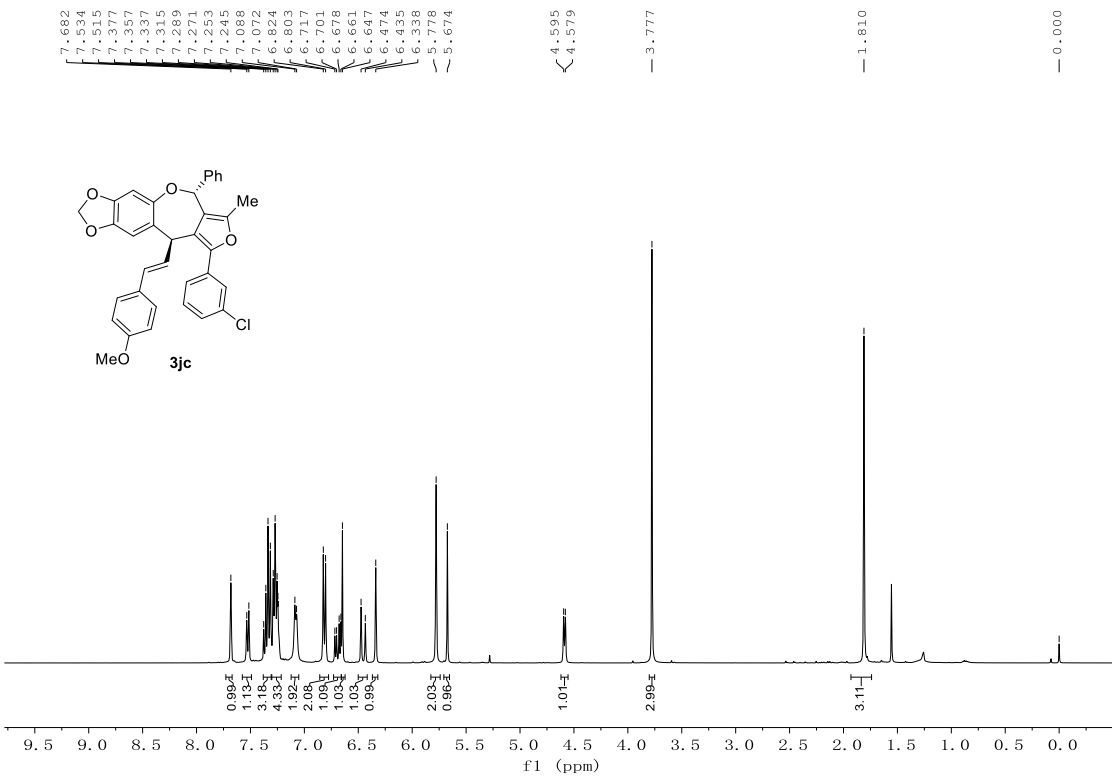
77.10
76.78
45.06
21.23
12.83
Ph
Me
Cl
Me
3jb
f1 (ppm)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6.803
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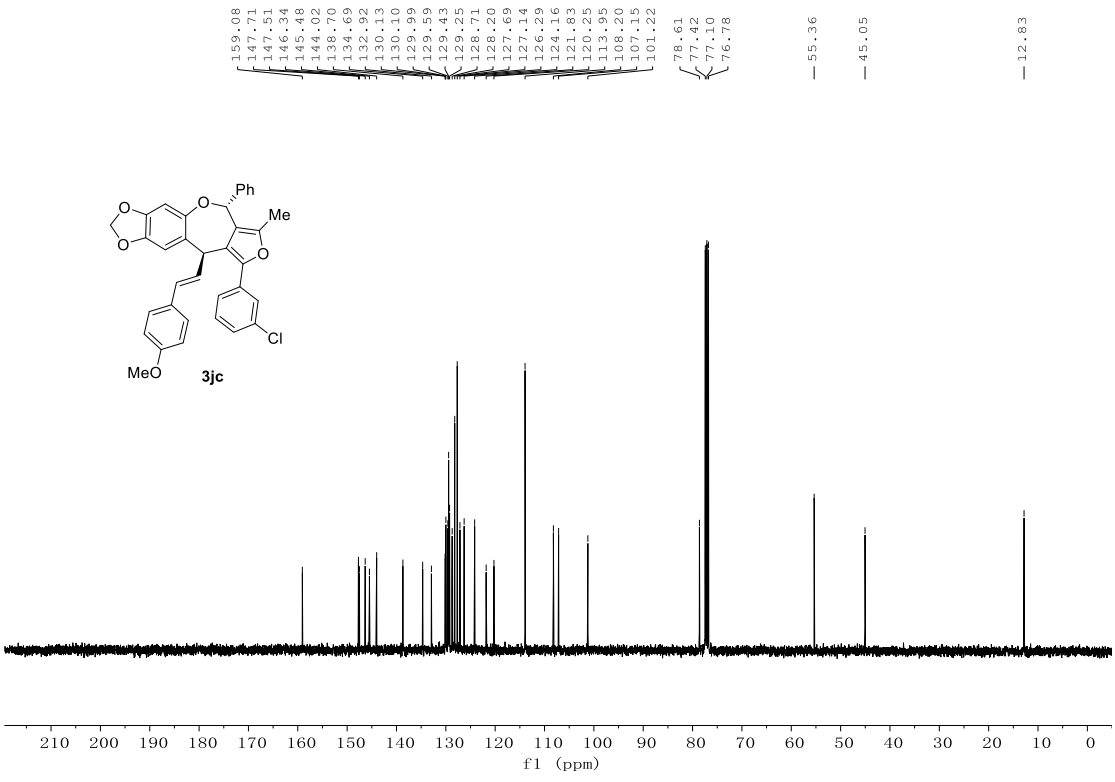
6.701
6.678
6.661
6.647
6.474
6.435
6.338
5.778
5.674
4.595
4.579
3.777
1.810
0.000
Ph
Me
O
O
O
O
Cl
MeO
3jc
0.99
1.13
3.18
4.33
1.92
2.08
1.09
1.03
1.03
0.99
2.03
0.96
1.01
2.99
3.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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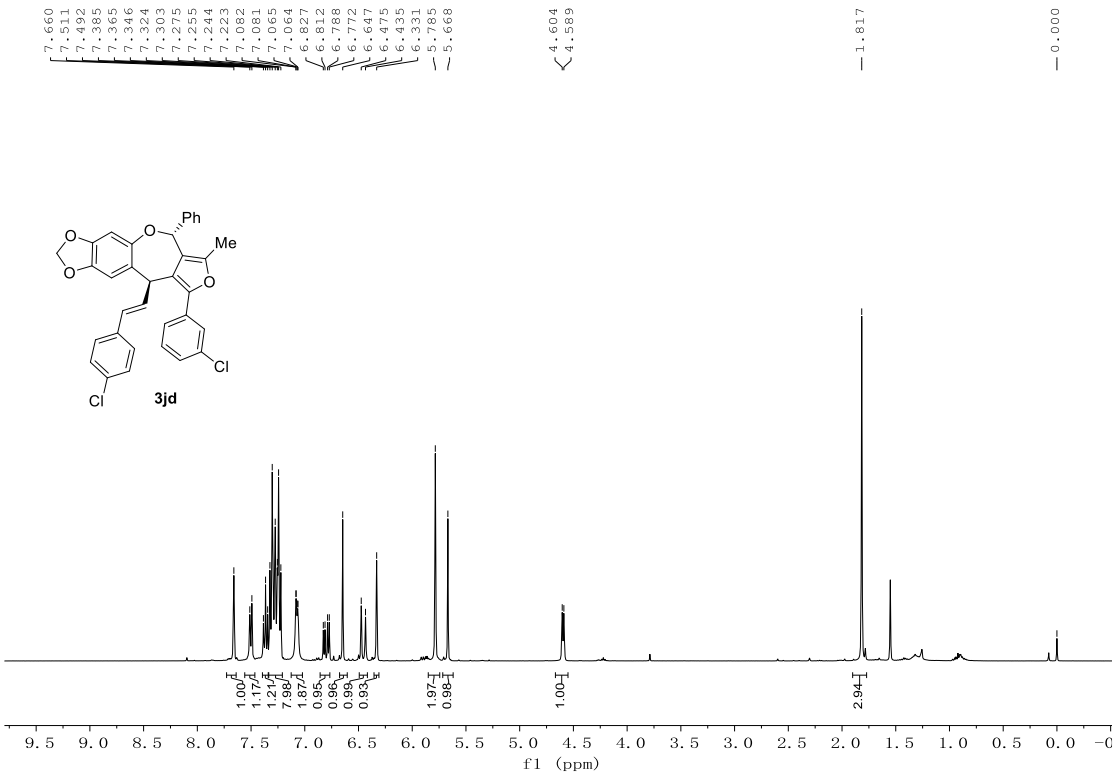
129.25
128.71
128.20
127.69
127.14
126.29
124.16
121.83
120.25
113.95
108.20
107.15
101.22
78.61
77.42
77.10
76.78
55.36
45.05
12.83
Ph
Me
O
O
O
O
Cl
MeO
3jc
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.303
7.275
7.255
7.244
7.223
7.082
7.081
7.065
7.064
6.827
6.812
6.788
6.772
6.647
6.475
6.435
6.331
5.785
5.668
4.604
4.589
1.817
0.000
Ph
Me
O
O
O
O
Cl
Cl
3jd
1.00
1.17
1.21
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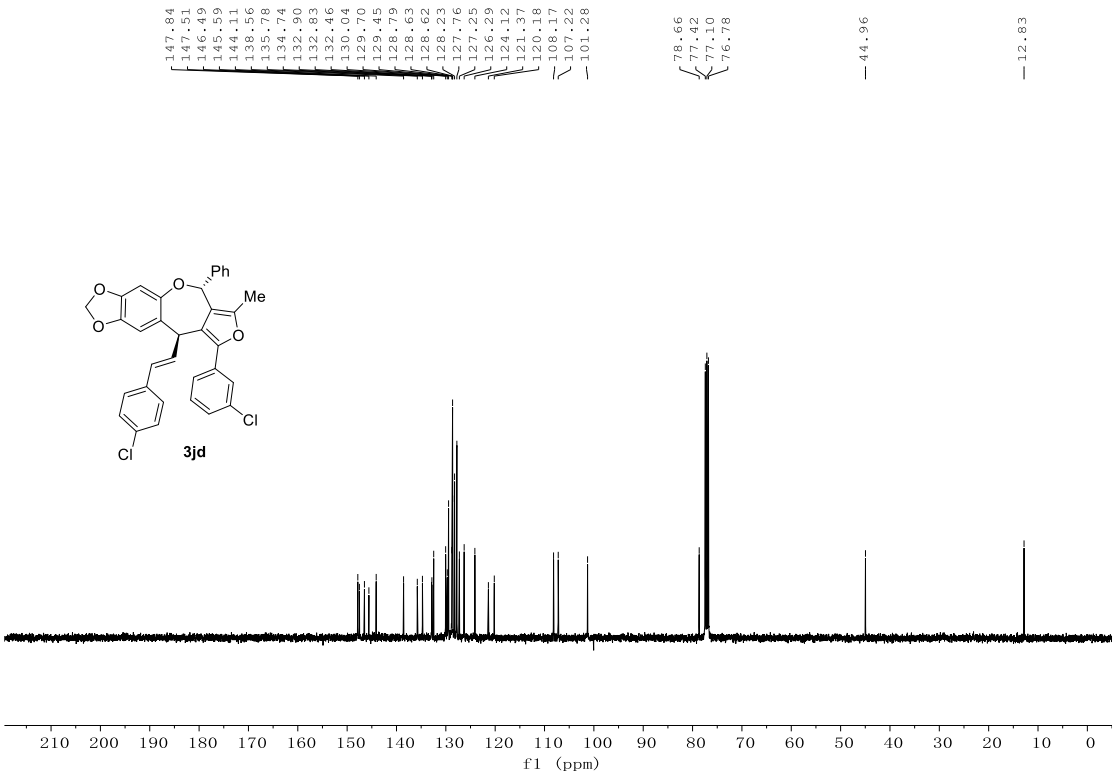
0.95
0.96
0.99
0.93
1.97
0.98
1.00
2.94
f1 (ppm)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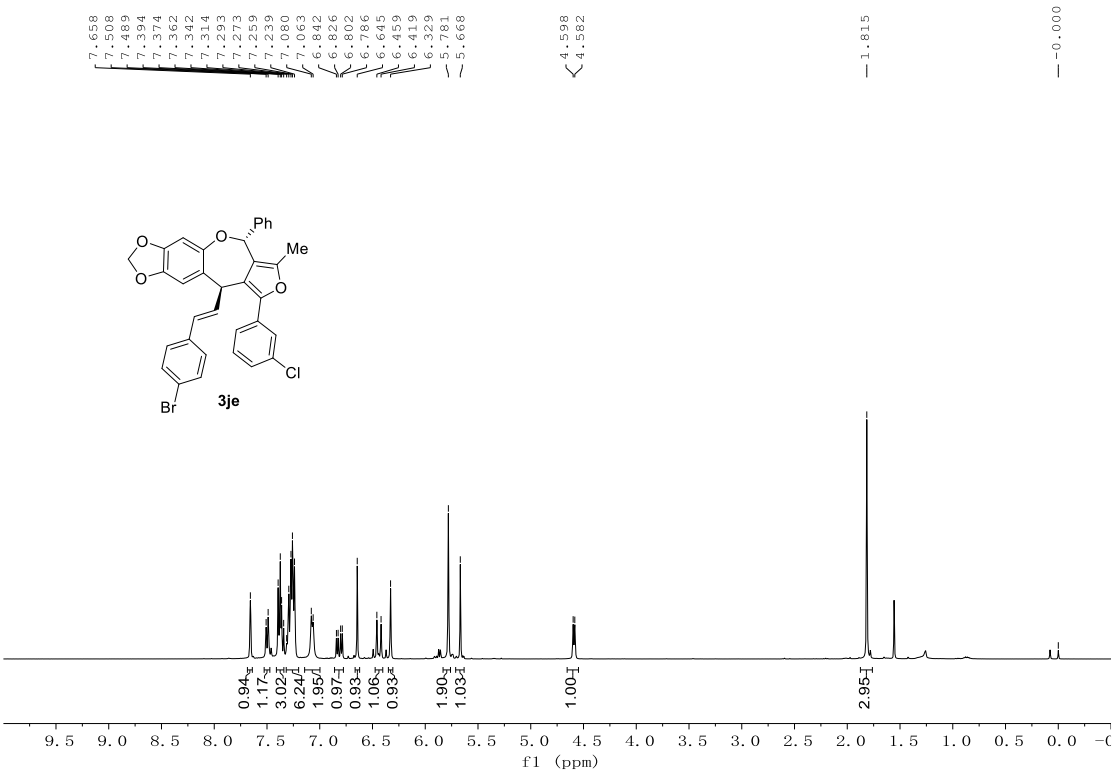
132.46
130.04
129.70
129.45
128.79
128.63
128.62
128.23
127.76
127.25
126.29
124.12
121.37
120.18
108.17
107.22
101.28
78.66
77.42
77.10
76.78
44.96
12.83
Ph
Me
O
O
O
O
Cl
Cl
3jd
f1 (ppm)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7.273
7.259
7.239
7.080
7.063
6.842
6.826
6.802
6.786
6.645
6.459
6.419
6.329
5.781
5.668
4.598
4.582
1.815
-0.000
Ph
Me
O
O
O
O
Cl
Br
3je
0.94
1.17
3.02
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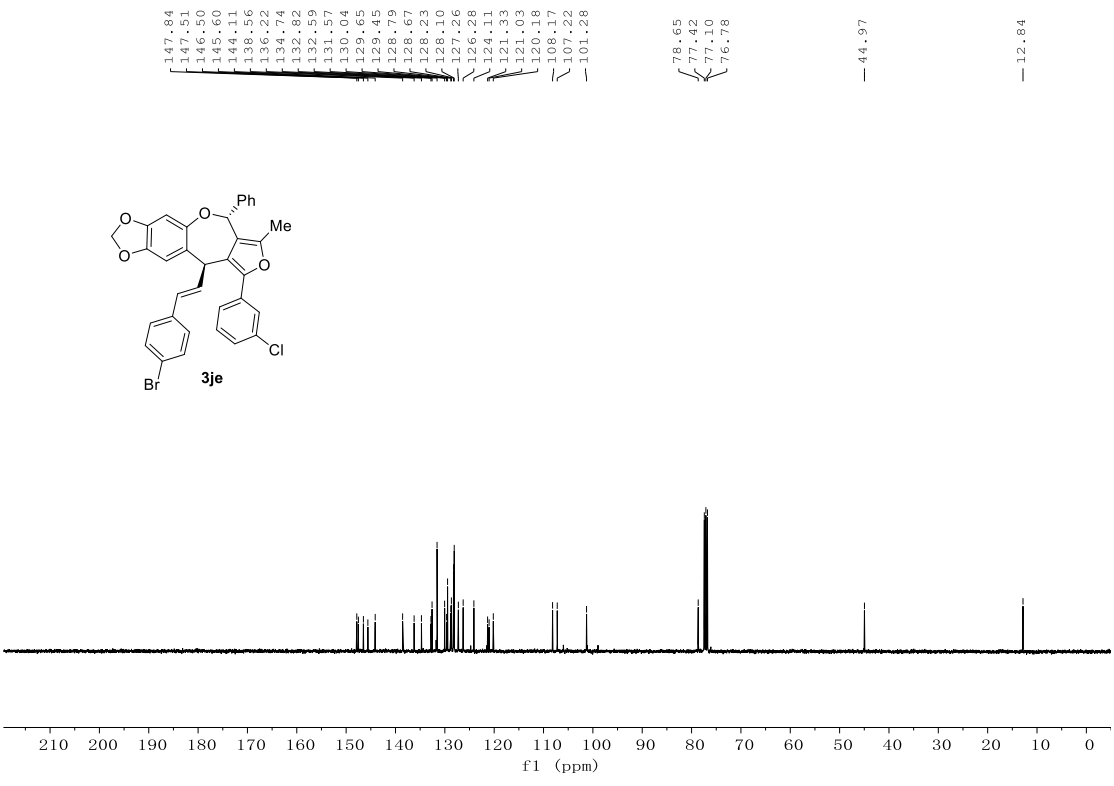
0.97
0.93
1.06
0.93
1.90
1.03
1.00
2.95
f1 (ppm)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129.45
128.79
128.67
128.23
128.10
127.26
126.28
124.11
121.33
121.03
120.18
108.17
107.22
101.28
78.65
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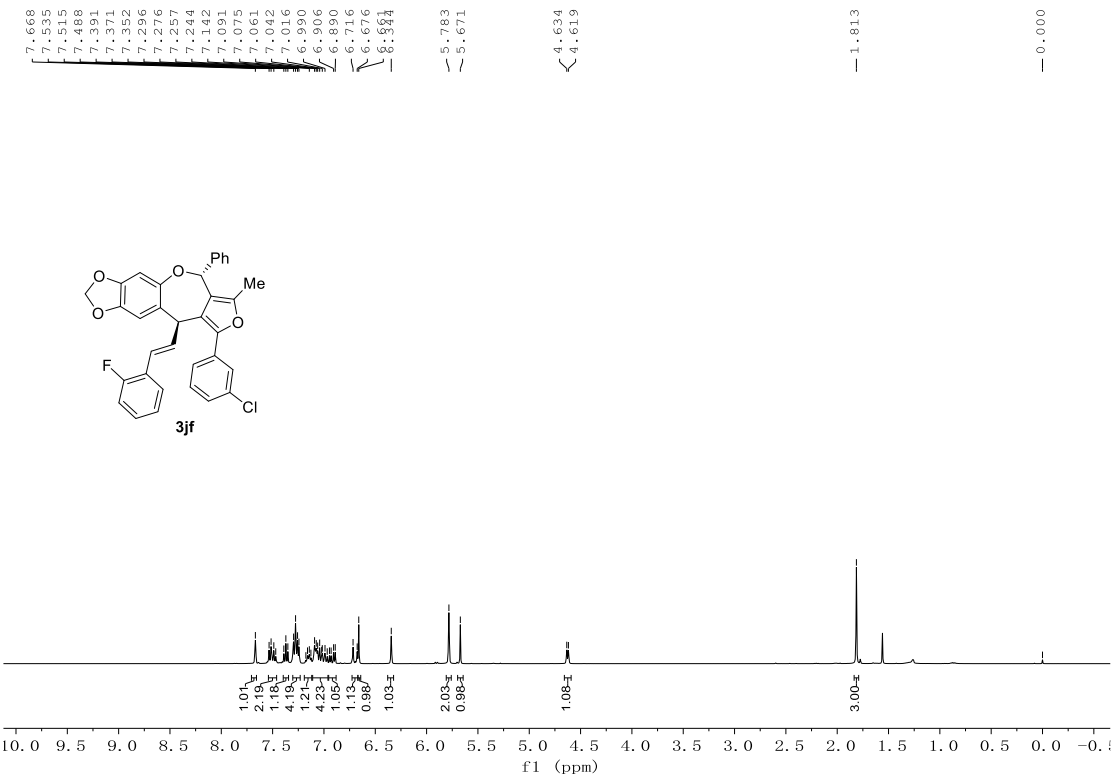
77.10
76.78
44.97
12.84
Ph
Me
O
O
O
O
Cl
Br
3je
f1 (ppm)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7.371
7.352
7.296
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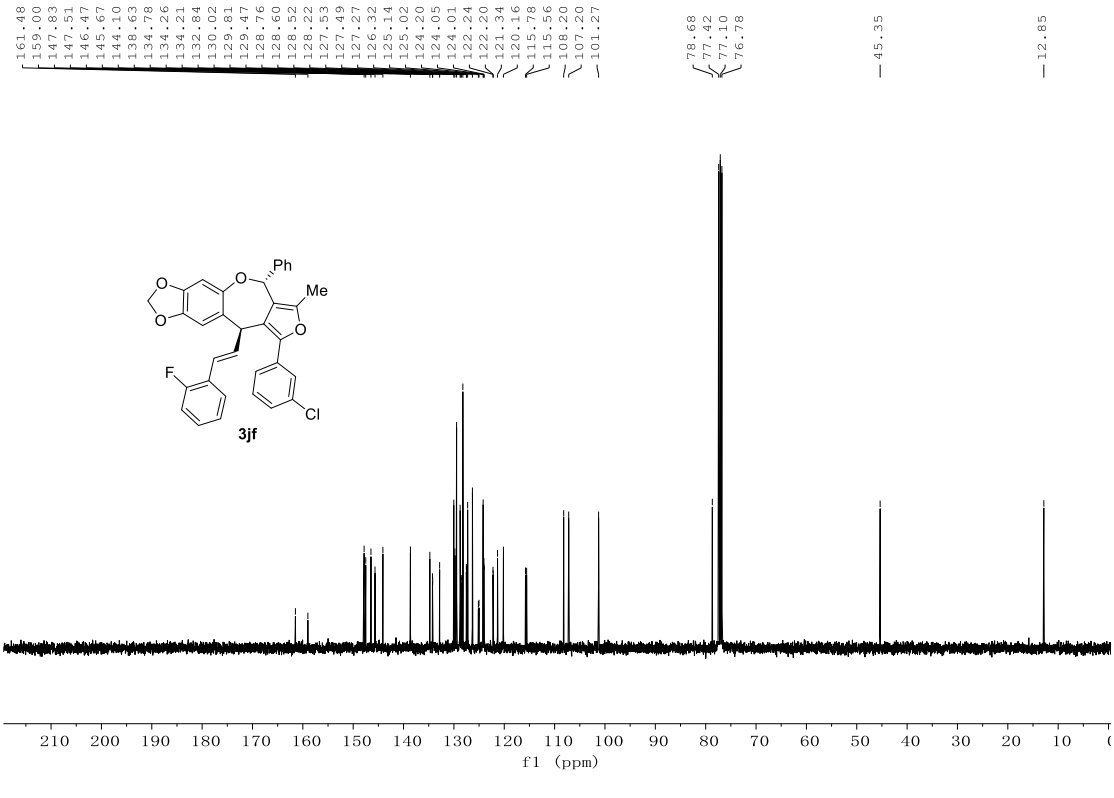
7.257
7.244
7.142
7.091
7.075
7.061
7.042
7.016
6.990
6.906
6.890
6.716
6.676
5.783
5.671
4.634
4.619
1.813
0.000
Ph
Me
O
O
O
O
F
Cl
3jf
1.01
2.19
1.18
4.19
1.21
4.23
1.05
1.13
0.98
1.03
2.03
0.98
1.08
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.81
129.47
128.76
128.60
128.52
128.22
127.53
127.49
127.27
126.32
125.14
125.02
124.20
124.05
124.01
122.24
122.20
121.34
120.16
115.78
115.56
108.20
107.20
101.27
78.68
77.42
77.10
76.78
45.35
12.85
Ph
Me
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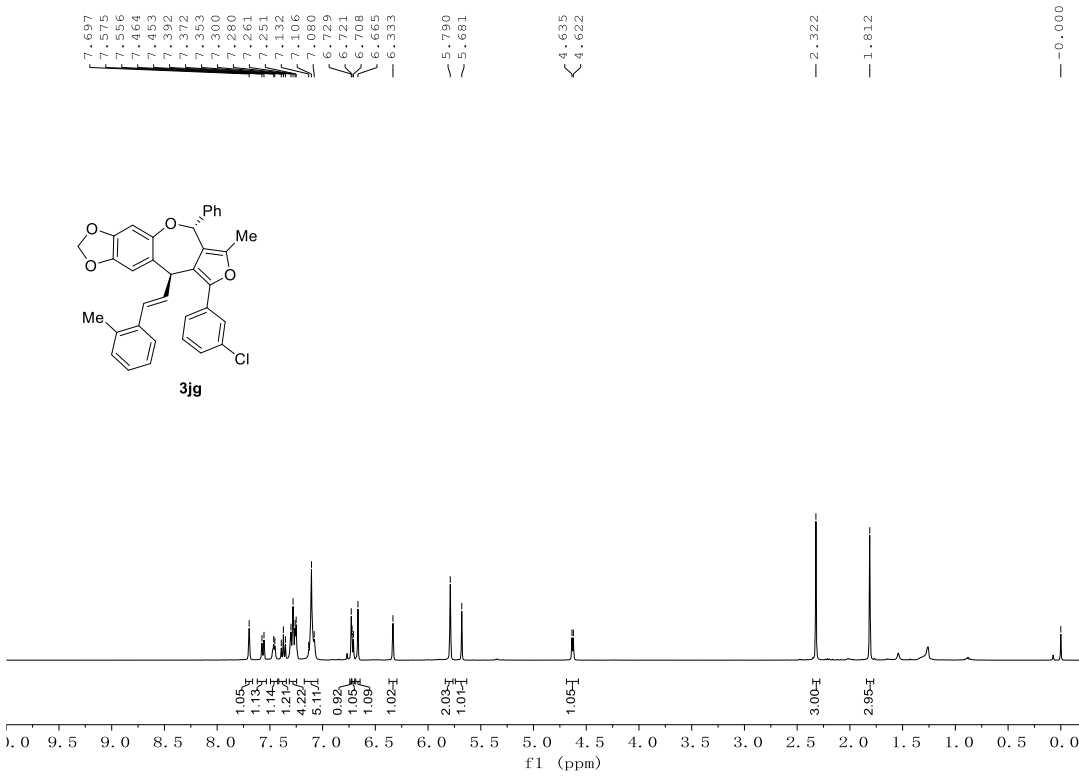
O
O
O
F
Cl
3jf
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.251
7.132
7.106
7.080
6.729
6.721
6.708
6.665
6.333
5.790
5.681
4.635
4.622
2.322
1.812
-0.000
Ph
Me
Me
Cl
3jg
1.05
1.13
1.14
1.21
4.22
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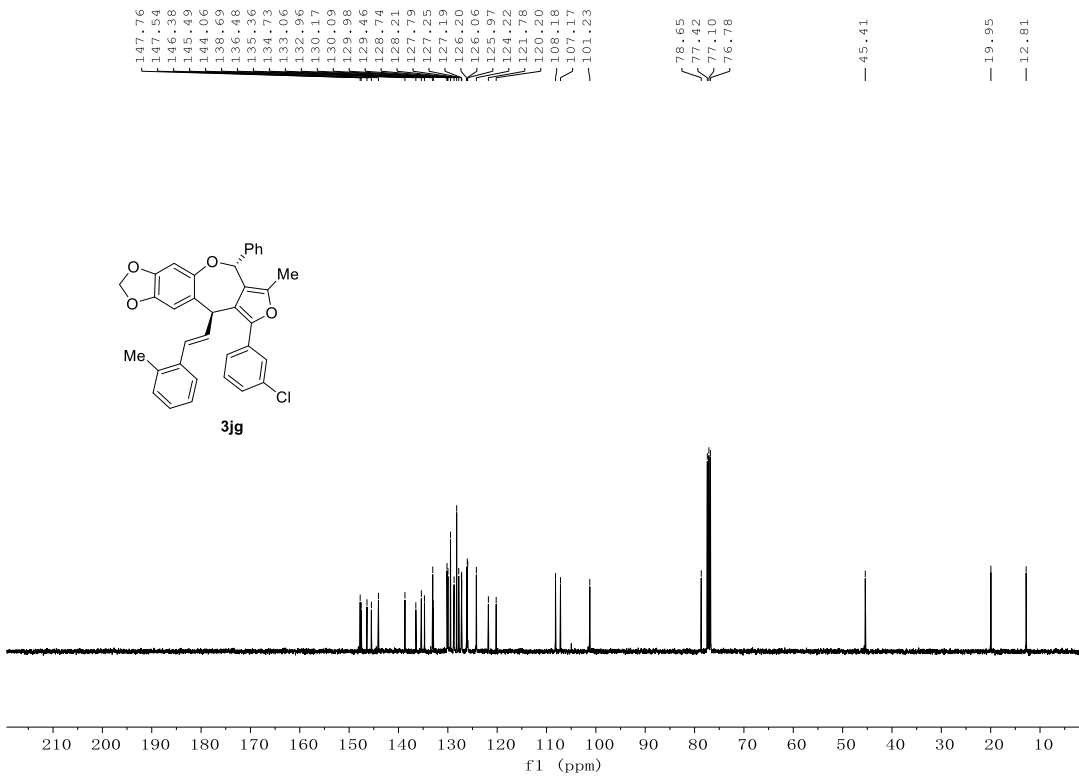
1.05
1.09
1.02
2.03
1.01
1.05
3.00
2.95
f1 (ppm)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130.09
129.98
129.46
128.74
128.21
127.79
127.25
127.19
126.20
126.06
125.97
124.22
121.78
120.20
108.18
107.17
101.23
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77.10
76.78
45.41
19.95
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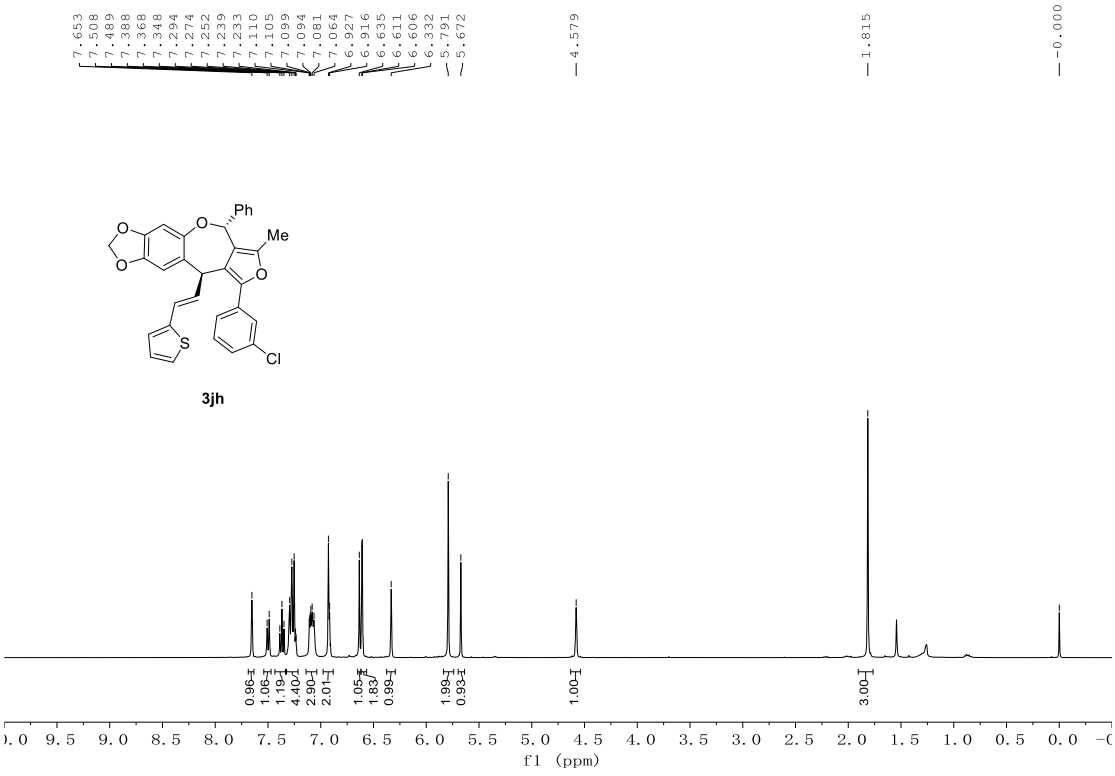
Ph
Me
Me
Cl
3jg
f1 (ppm)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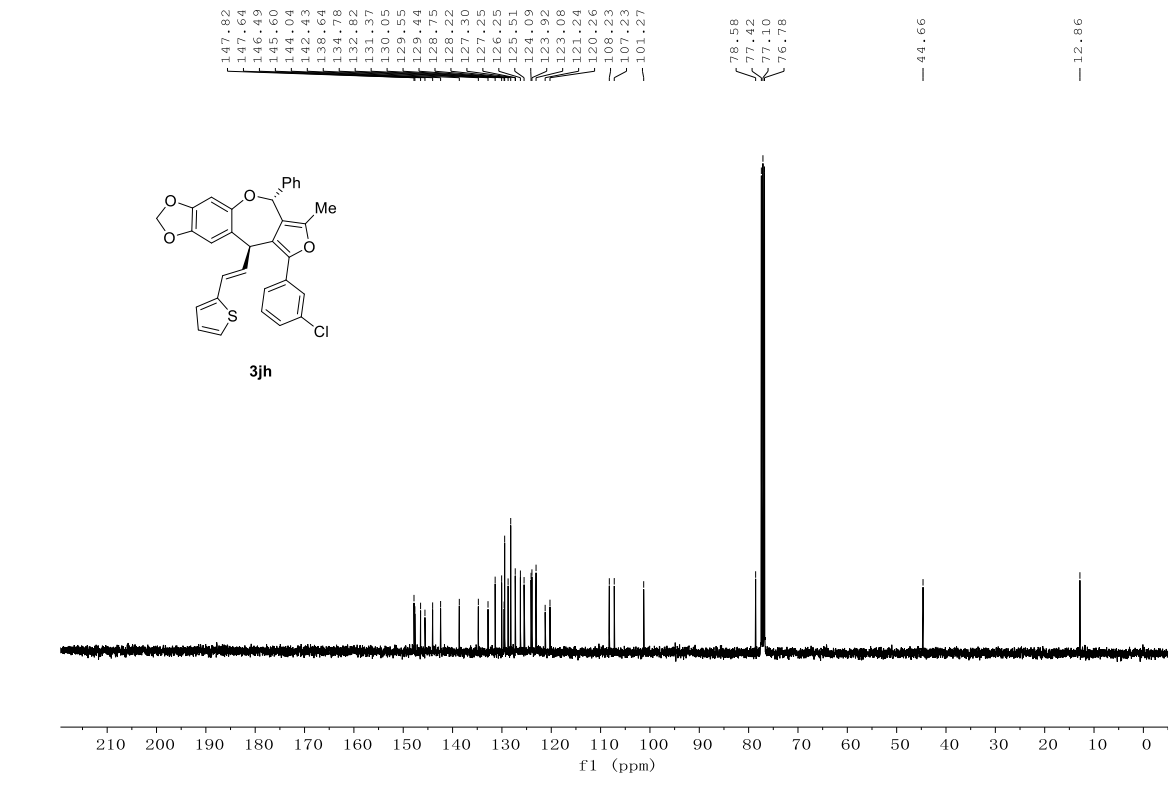
7.239
7.233
7.110
7.105
7.099
7.094
7.081
7.064
6.327
6.316
6.635
6.611
6.606
6.332
5.791
5.672
4.579
1.815
-0.000
Ph
Me
O
S
Cl
0.96
1.06
1.19
4.40
2.90
2.01
1.05
1.83
0.99
1.99
0.93
1.00
3.00
f1 (ppm)

3jh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129.55
129.44
128.75
128.22
127.30
127.25
126.25
125.51
124.09
123.92
123.08
121.24
120.26
108.23
107.23
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77.10
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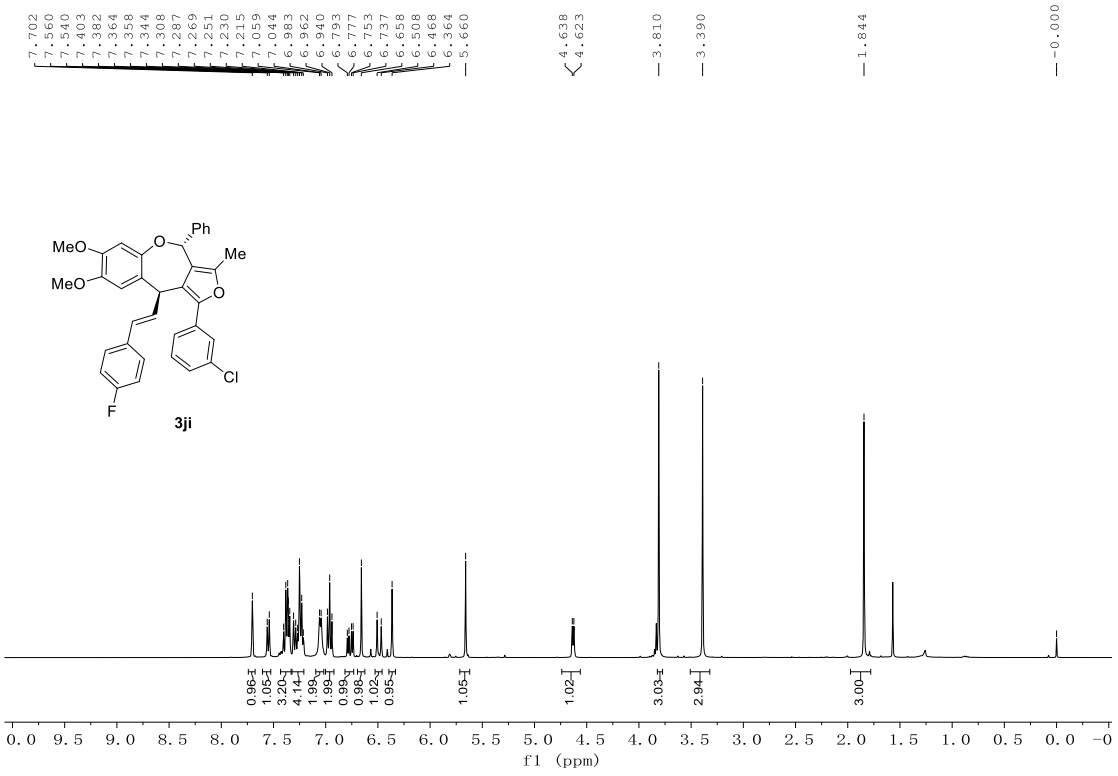
Ph
Me
O
S
Cl
f1 (ppm)

3jh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7.230
7.215
7.059
7.044
6.983
6.962
6.940
6.793
6.777
6.753
6.737
6.658
6.508
6.468
6.364
5.660
4.638
4.623
3.810
3.390
1.844
-0.000
MeO
MeO
O
Ph
Me
O
Cl
F
3ji
0.96
1.05
3.20
4.14
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1.99
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0.98
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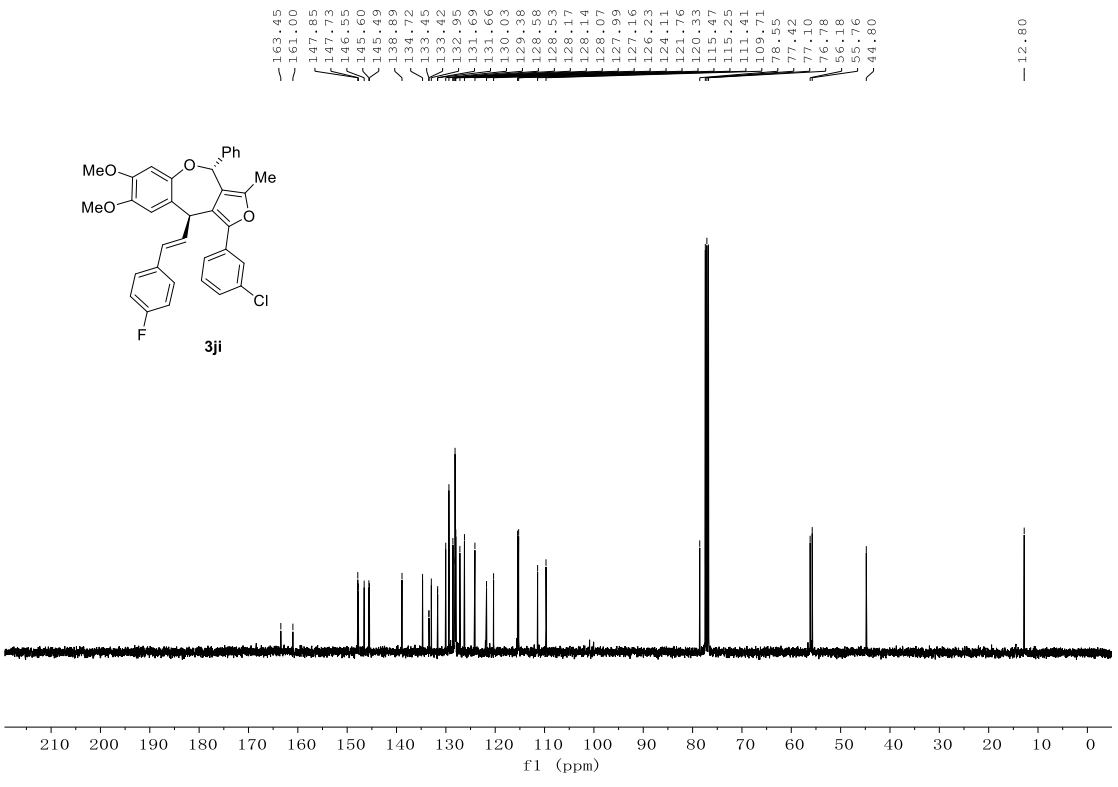
1.02
3.03
2.94
3.00
f1 (ppm)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131.69
131.66
130.03
129.38
128.58
128.53
128.17
128.14
128.07
127.99
127.16
126.23
124.11
121.76
120.33
115.47
115.25
111.41
109.71
78.55
77.42
77.10
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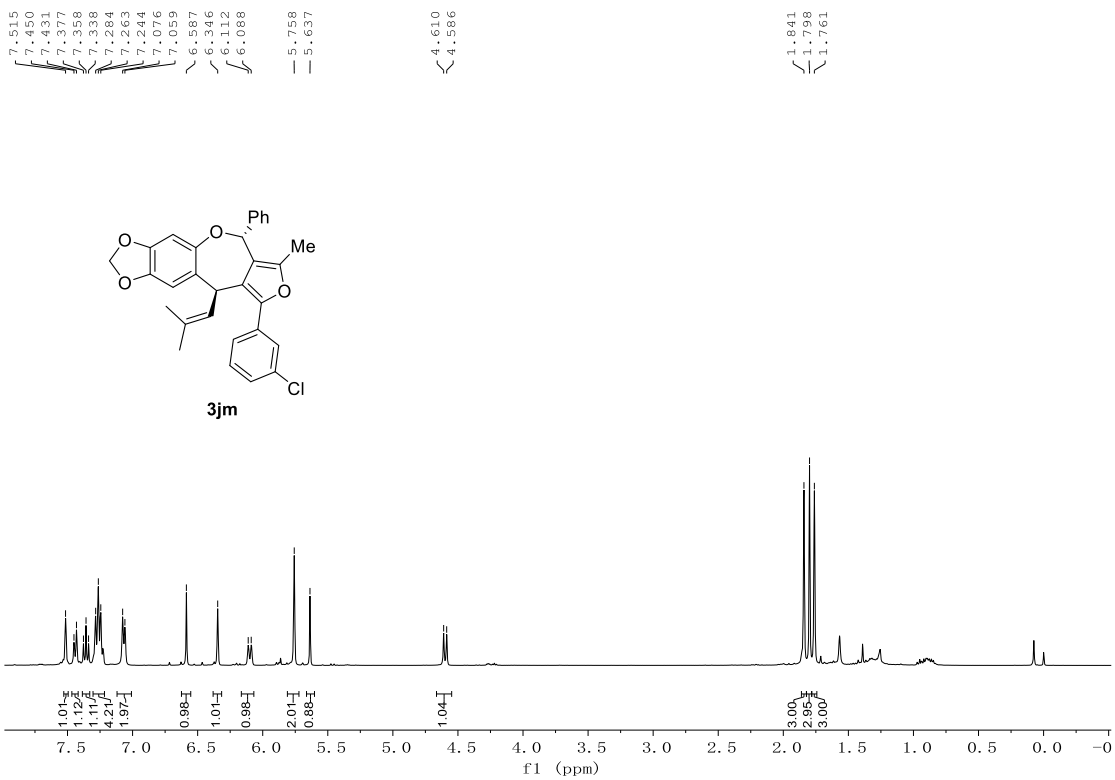
MeO
O
Ph
Me
O
Cl
F
3ji
f1 (ppm)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7.263
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7.076
7.059
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6.112
6.088
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5.637
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1.841
1.798
1.761
Ph
Me
O
O
O
Cl
3jm
1.01
1.12
1.11
4.21
1.97
0.98
1.01
0.98
2.01
0.88
1.04
3.00
2.95
3.00
7.5
7.0
6.5
6.0
5.5
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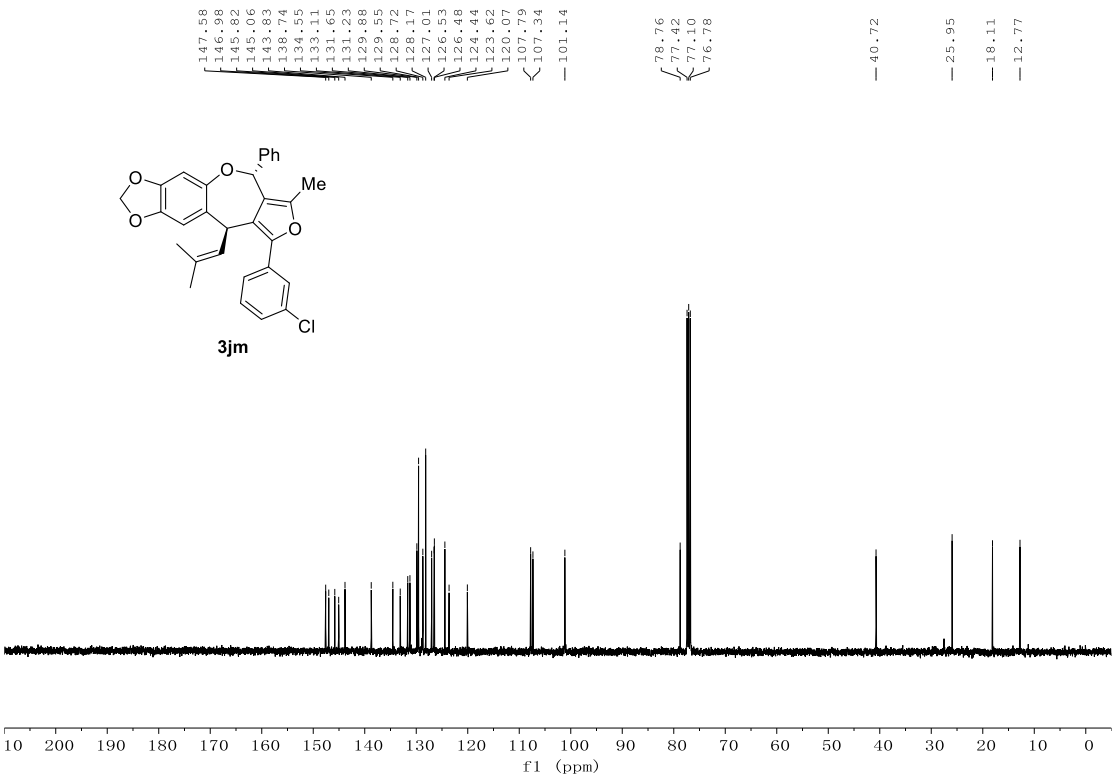
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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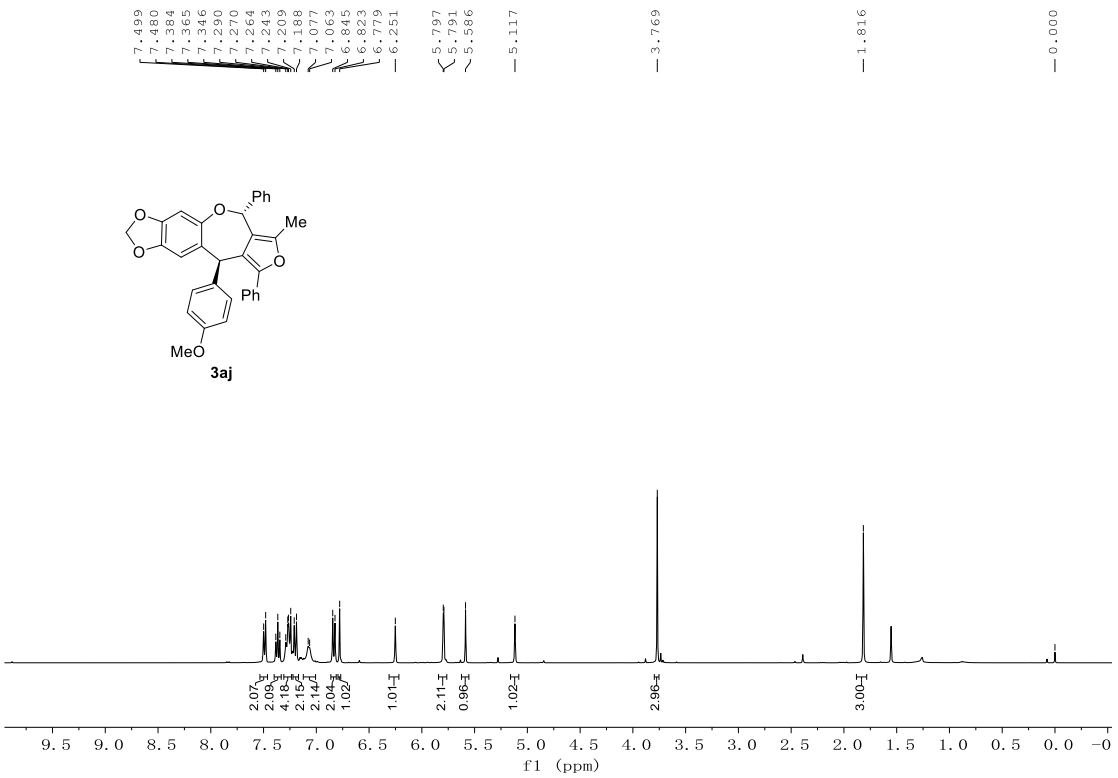
145.06
143.83
138.74
134.55
133.11
131.65
131.23
129.88
129.55
128.72
128.17
127.01
126.53
126.48
124.44
123.62
120.07
107.79
107.34
101.14
78.76
77.42
77.10
76.78
40.72
25.95
18.11
12.77
Ph
Me
O
O
O
Cl
3jm
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.077
7.063
6.845
6.823
6.779
6.251
5.797
5.791
5.586
5.117
3.769
1.816
0.000
Ph
Me
Ph
MeO
3aj
2.07
2.09
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2.04
1.02
1.01
2.11
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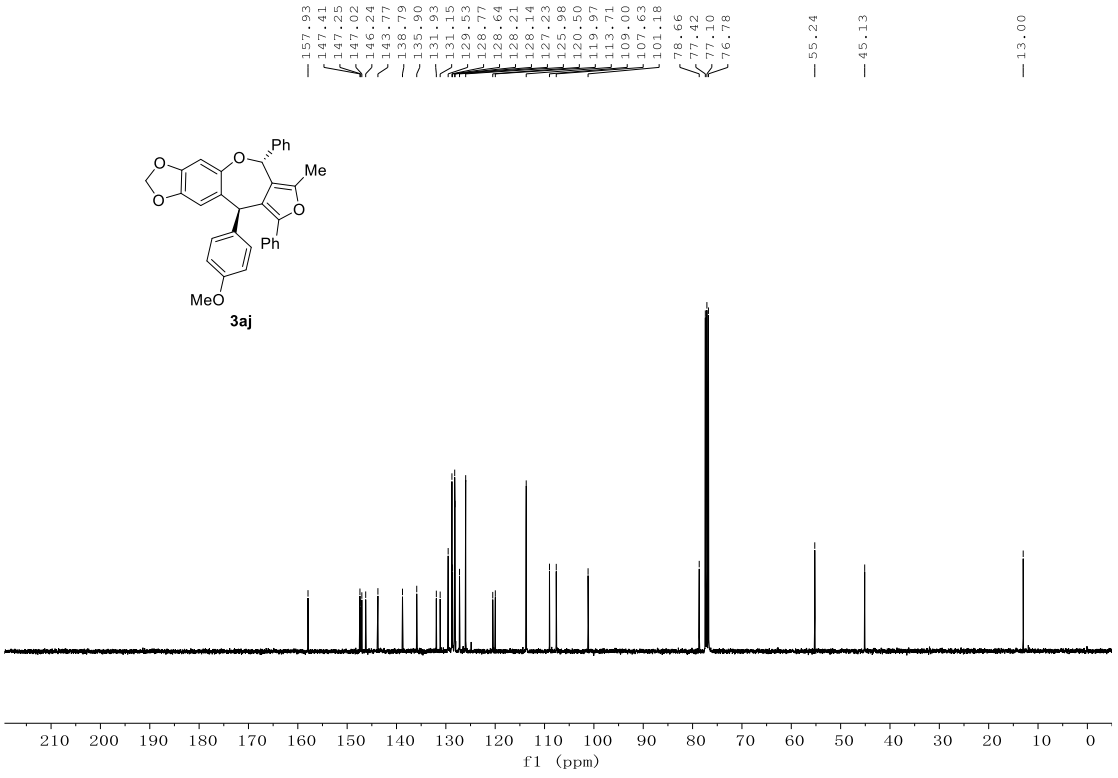
1.02
2.96
3.00
f1 (ppm)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143.77
138.79
135.90
131.93
131.15
129.53
128.77
128.64
128.21
128.14
127.23
125.98
120.50
119.97
113.71
109.00
107.63
101.18
78.66
77.42
77.10
76.78
55.24
45.13
13.00
Ph
Me
Ph
MeO
3aj
f1 (ppm)


7.389
7.369
7.299
7.283
7.258
7.245
7.229
7.199
7.188
7.177
7.168
7.076
7.066
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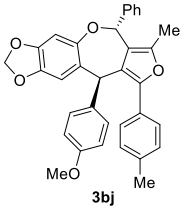
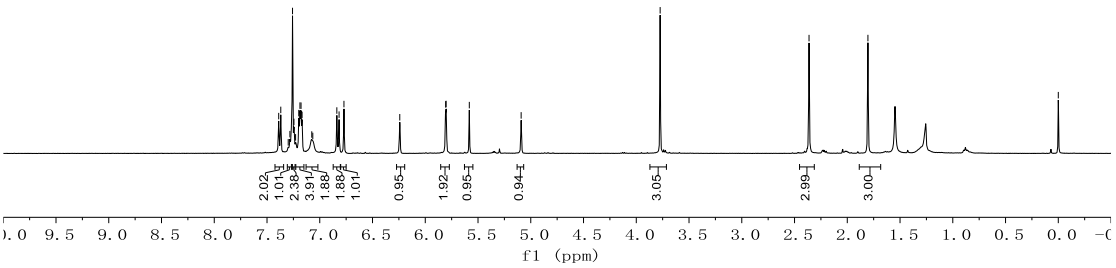
-0.000


Ph
Me
O
O
O
O
MeO
Me

3bj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1.88
1.88
1.01
0.95
1.92
0.95
0.94
3.05
2.99
3.00
f1 (ppm)


157.90
147.44
147.05
147.01
146.20
143.74
138.85
137.07
136.04
132.01
129.54
129.46
128.61
128.40
128.21
128.12
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119.86
119.83
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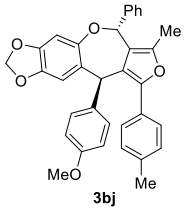
12.99


Ph
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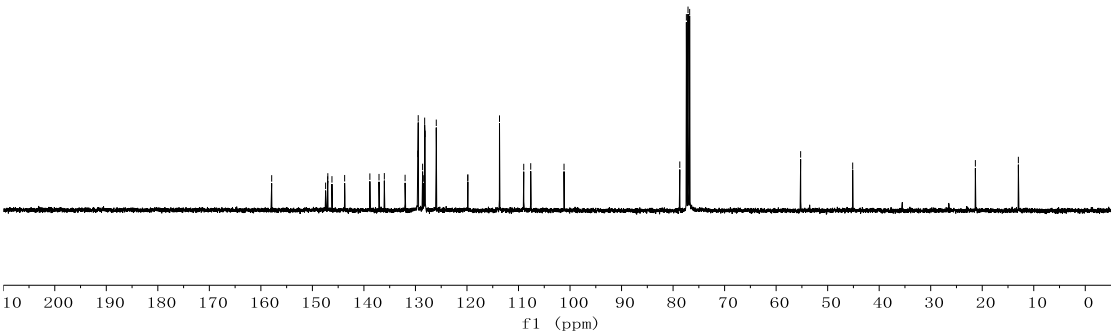
O
O
O
O
MeO
Me

3bj


f1 (ppm)


7.500
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7.352
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7.289
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7.248
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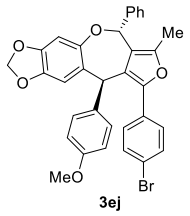
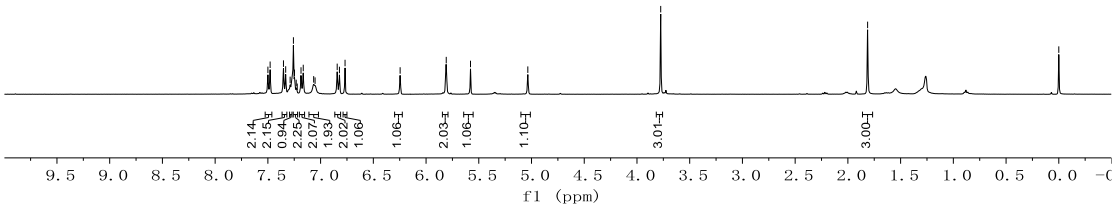
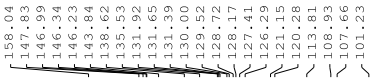
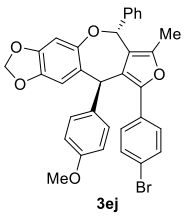

Ph
Me
O
O
O
O
MeO
Br

3ej

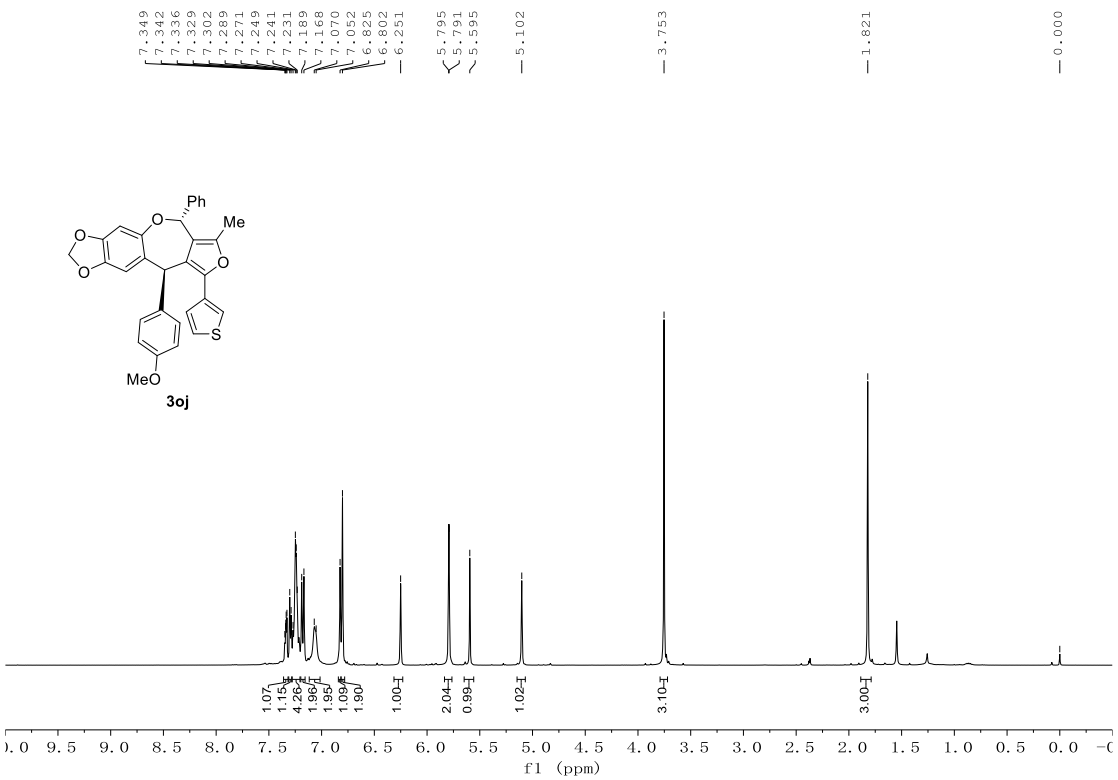

2.14
2.15
0.94
2.25
2.07
1.93
2.02
1.06
1.06
2.03
1.06
1.10
3.01
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

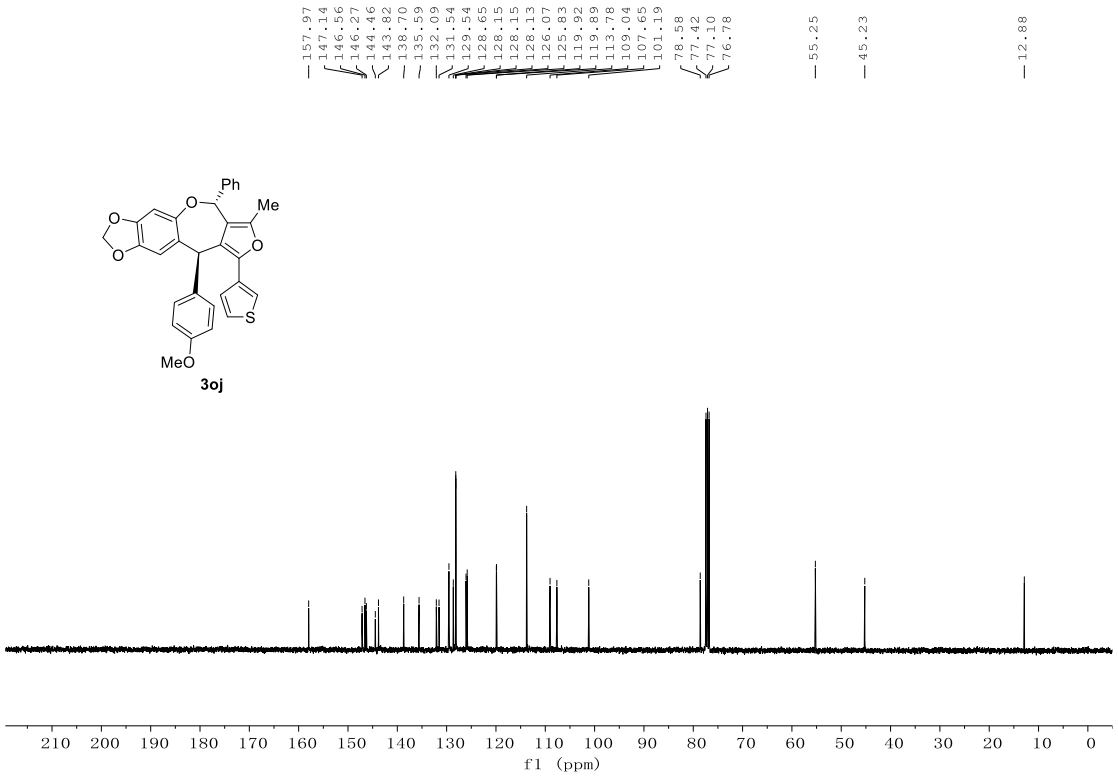

158.04
147.83
146.99
146.34
146.23
143.84
138.62
135.53
131.92
131.65
131.39
130.00
129.52
128.72
128.17
127.41
126.29
121.15
120.28
113.81
108.93
107.66
101.23
78.59
77.42
77.10
76.78
55.26
45.25
13.01

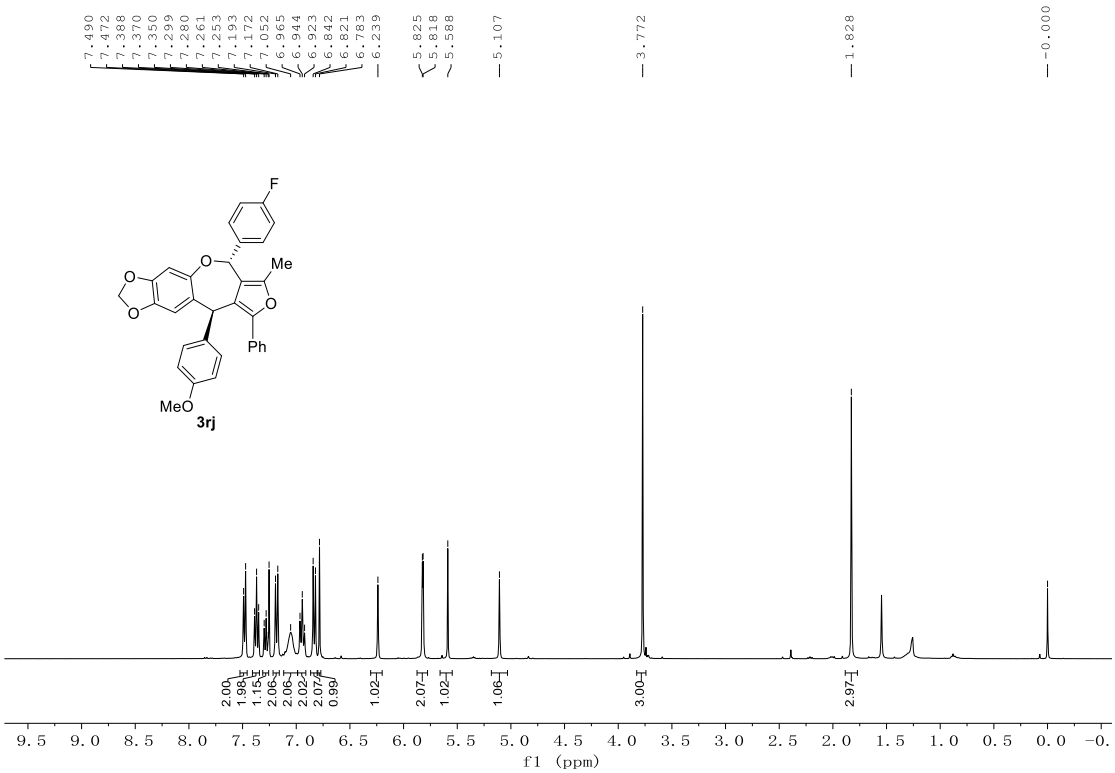

Ph
Me
O
O
O
O
MeO
Br

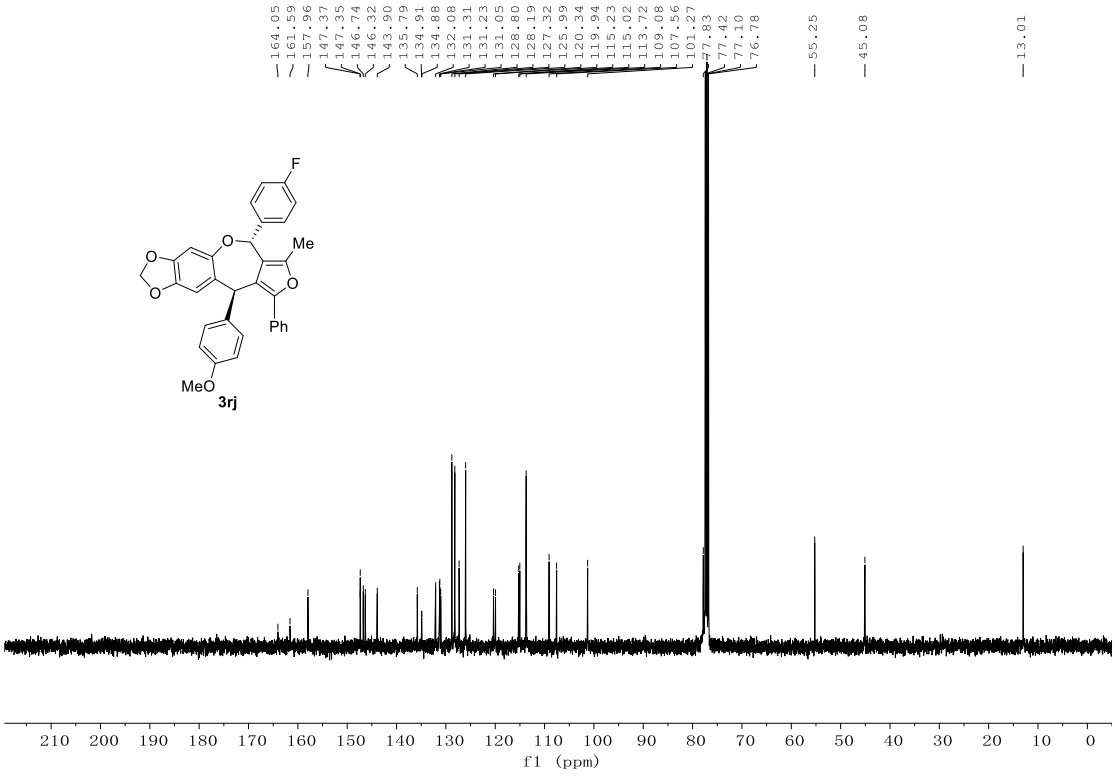
3ej

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

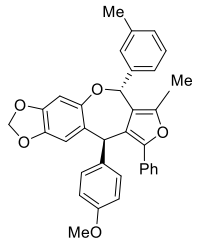

7.349
7.342
7.336
7.329
7.302
7.289
7.271
7.249
7.241
7.231
7.189
7.168
7.070
7.052
6.825
6.802
6.251
5.795
5.791
5.595
5.102
3.753
1.821
0.000
Ph
Me
O
O
O
O
S
MeO
3oj
1.07
1.15
4.26
1.96
1.95
1.09
1.90
1.00
2.04
0.99
1.02
3.10
3.00
f1 (ppm)


157.97
147.14
146.56
146.27
144.46
143.82
138.70
135.59
132.09
131.54
129.54
128.65
128.15
128.15
128.13
126.07
125.83
119.92
119.89
113.78
109.04
107.65
101.19
78.58
77.42
77.10
76.78
55.25
45.23
12.88
Ph
Me
O
O
O
O
S
MeO
3oj
f1 (ppm)

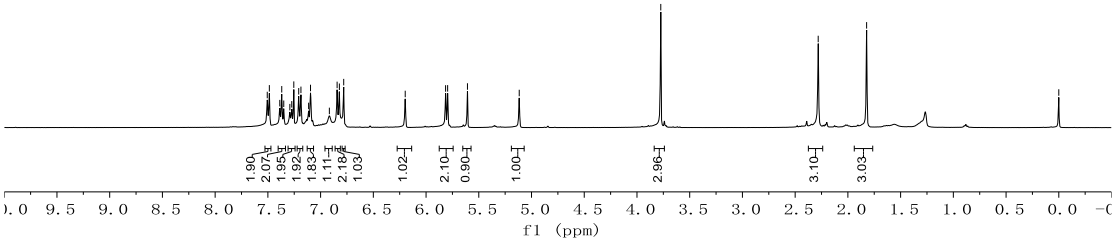

7.490
7.472
7.388
7.370
7.350
7.299
7.280
7.261
7.253
7.193
7.172
7.052
6.965
6.944
6.923
6.842
6.821
6.783
6.239
5.825
5.818
5.588
5.107
3.772
1.828
-0.000
F
Me
O
Ph
MeO
3rj
2.00
1.98
1.15
2.06
2.02
2.07
0.99
1.02
2.07
1.02
1.06
3.00
2.97
f1 (ppm)

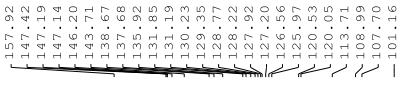

164.05
161.59
157.96
147.37
147.35
146.74
146.32
143.90
135.79
134.91
134.88
132.08
131.31
131.23
131.05
128.80
128.19
127.32
125.99
120.34
119.94
115.23
115.02
113.72
109.08
107.56
101.27
77.83
77.42
77.10
76.78
55.25
45.08
13.01
F
Me
O
Ph
MeO
3rj
f1 (ppm)

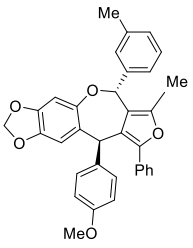

7.506
7.486
7.387
7.368
7.349
7.292
7.274
7.254
7.208
7.186
7.114
7.096
6.917
6.843
6.822
6.781
6.198
5.815
5.795
5.607
5.116
3.774
2.281
1.822
0.000


Me
Me
O
O
O
O
Ph
MeO

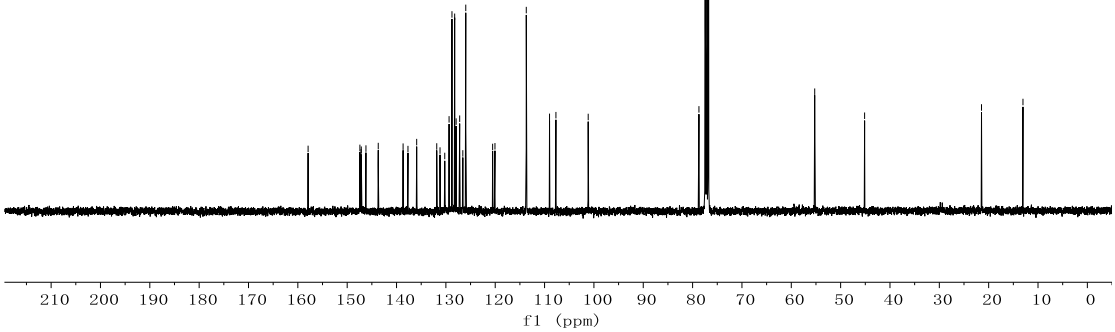
3sj


1.90
2.07
1.95
1.92
1.83
1.11
2.18
1.03
1.02
2.10
0.90
1.00
2.96
3.10
3.03
f1 (ppm)

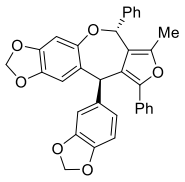

157.92
147.42
147.19
147.14
146.20
143.71
138.67
137.68
135.92
131.85
131.19
130.23
129.35
128.77
128.22
127.92
127.20
126.56
125.97
120.53
120.05
113.71
108.99
107.70
101.16
78.71
77.42
77.10
76.78
55.25
45.14
21.45
13.05


Me
Me
O
O
O
O
Ph
MeO

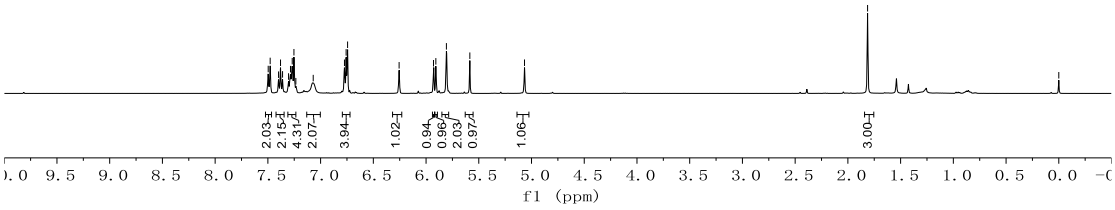
3sj


f1 (ppm)

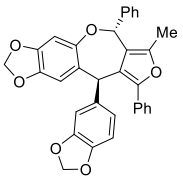

7.497
7.478
7.399
7.380
7.361
7.304
7.286
7.269
7.253
7.235
7.070
6.774
6.758
6.744
6.255
5.929
5.907
5.807
5.585
5.066
1.813
0.000


Ph
Me
O
O
O
O
Ph
O
O

3ak

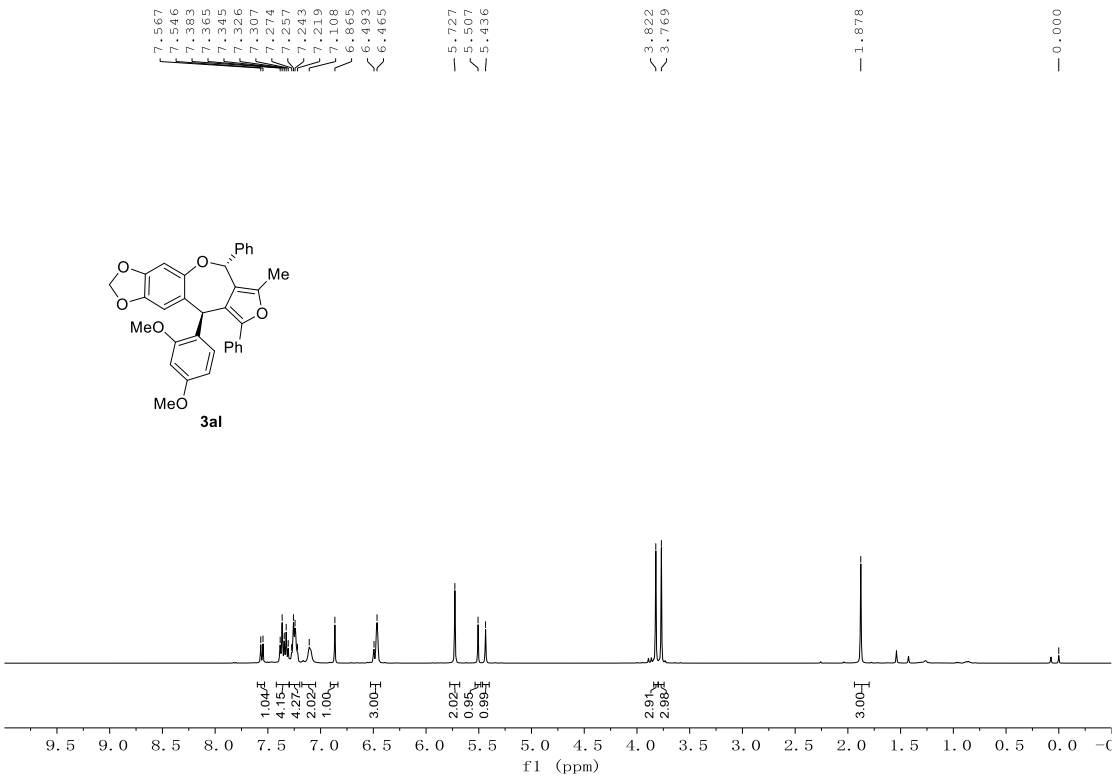

2.03
2.15
4.31
2.07
3.94
1.02
0.94
0.96
2.03
0.97
1.06
3.00
f1 (ppm)

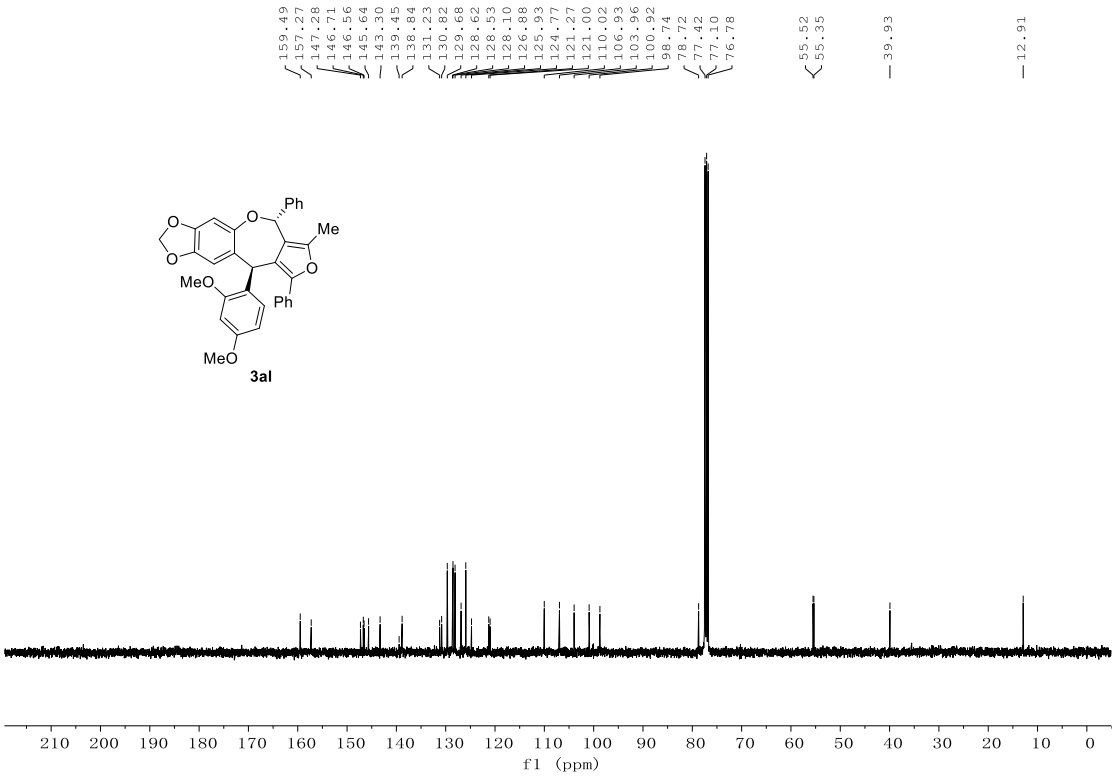

147.73
147.50
147.36
146.96
146.34
145.92
143.83
138.71
137.88
131.81
131.06
129.54
128.79
128.69
128.16
127.30
126.00
120.29
120.27
119.85
108.99
108.12
108.06
107.66
101.22
101.00
78.71
77.42
77.10
76.78
45.48
13.01

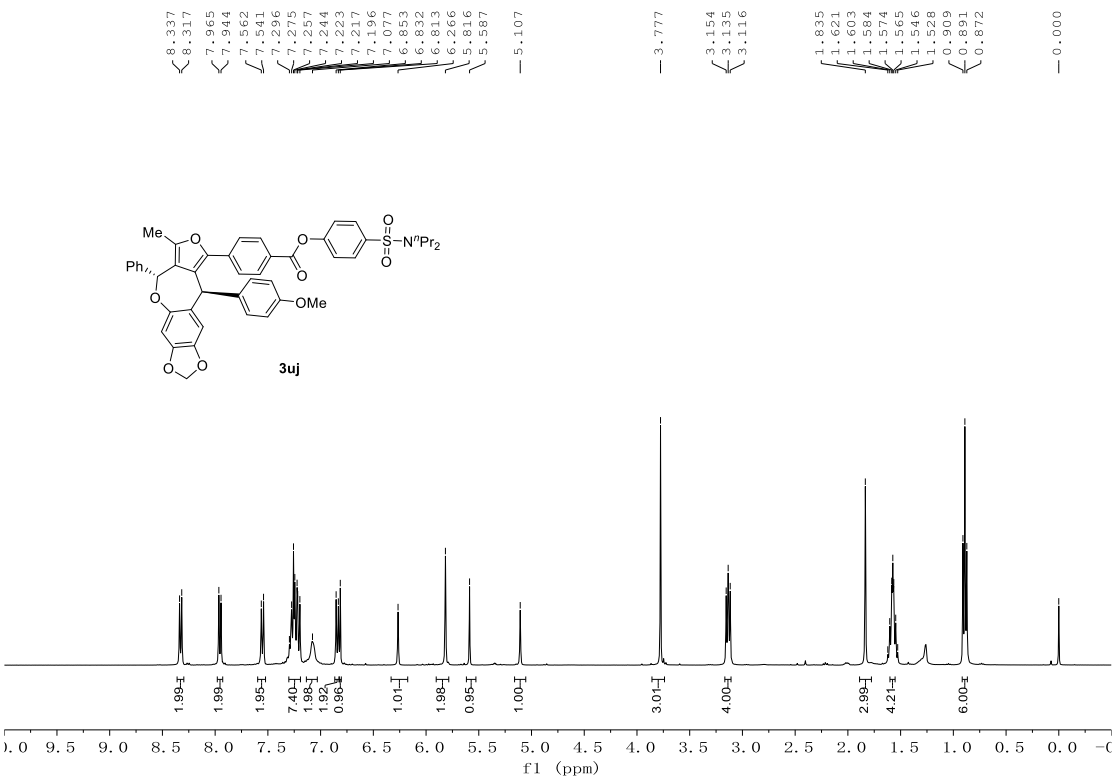

Ph
Me
O
O
O
O
Ph
O
O

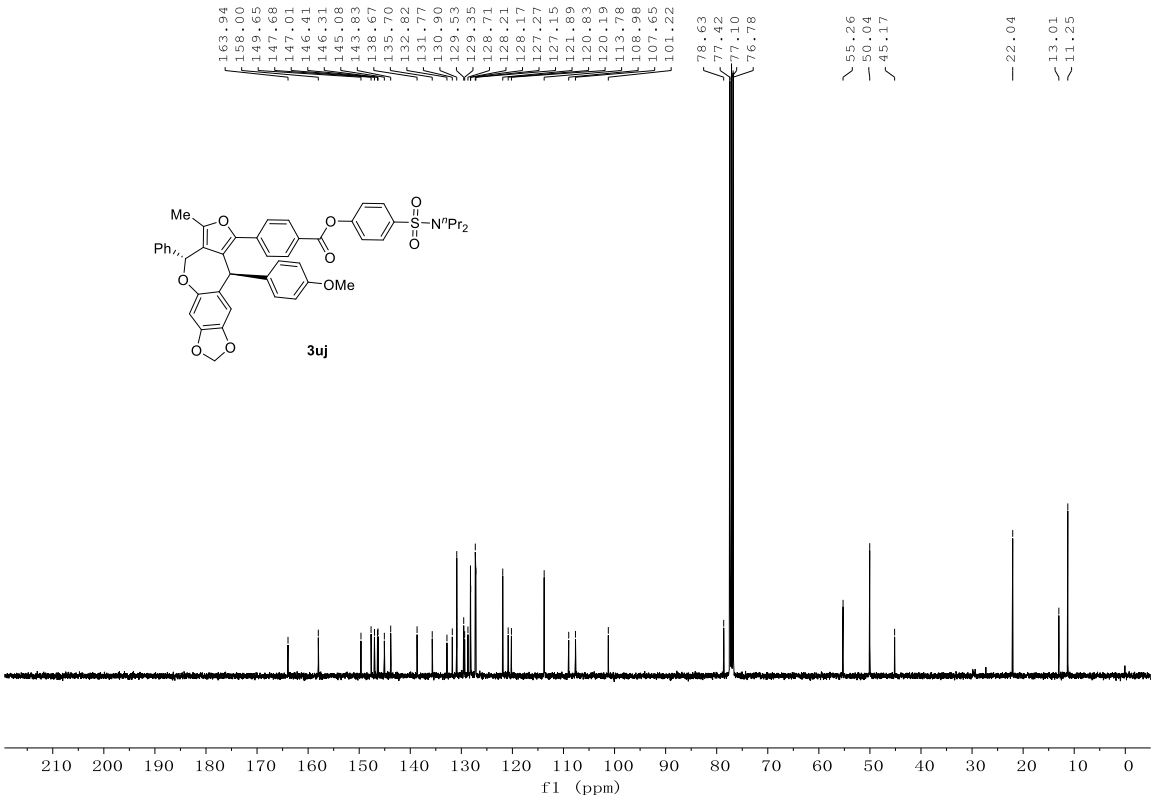
3ak

f1 (ppm)

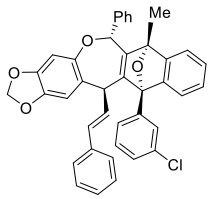

7.567
7.546
7.383
7.365
7.345
7.326
7.307
7.274
7.257
7.243
7.219
7.108
6.865
6.493
6.465
5.727
5.507
5.436
3.822
3.769
1.878
0.000
Ph
Me
O
O
O
MeO
Ph
MeO
3al
1.04
4.15
4.27
2.02
1.00
3.00
2.02
0.95
0.99
2.91
2.98
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


159.49
157.27
147.28
146.71
146.56
145.64
143.30
139.45
138.84
131.23
130.82
129.68
128.62
128.53
128.10
126.88
125.93
124.77
121.27
121.00
110.02
106.93
103.96
100.92
98.74
78.72
77.42
77.10
76.78
55.52
55.35
39.93
12.91
Ph
Me
O
O
O
MeO
Ph
MeO
3al
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

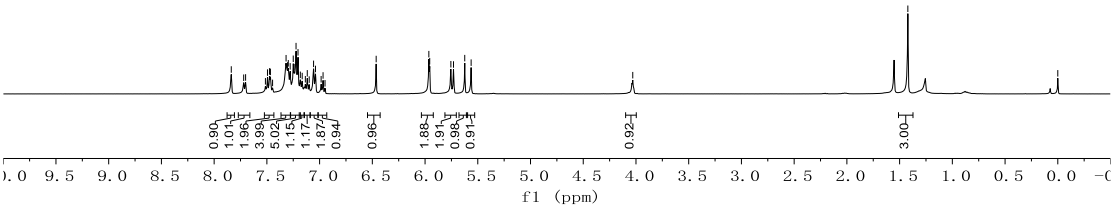

8.337
8.317
7.965
7.944
7.562
7.541
7.296
7.275
7.257
7.244
7.223
7.217
7.196
7.077
6.853
6.832
6.813
6.266
5.816
5.587
5.107
3.777
3.154
3.135
3.116
1.835
1.621
1.603
1.584
1.574
1.565
1.546
1.528
0.909
0.891
0.872
0.000
Me
Ph
O
O
O
O
O
S
O
N^{n}Pr$_2$
OMe
O
O
3uj
1.99
1.99
1.95
7.40
1.98
1.92
0.96
1.01
1.98
0.95
1.00
3.01
4.00
2.99
4.21
6.00
f1 (ppm)

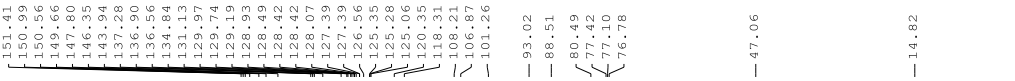

163.94
158.00
149.65
147.68
147.01
146.41
146.31
145.08
143.83
138.67
135.70
132.82
131.77
130.90
129.53
129.35
128.71
128.21
128.17
127.27
127.15
121.89
120.83
120.19
113.78
108.98
107.65
101.22
78.63
77.42
77.10
76.78
55.26
50.04
45.17
22.04
13.01
11.25
Me
Ph
O
O
O
O
O
S
O
N^{n}Pr$_2$
OMe
O
O
3uj
f1 (ppm)

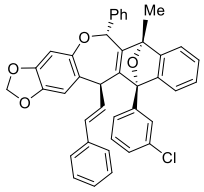

7.838
7.720
7.702
7.494
7.475
7.466
7.318
7.304
7.297
7.279
7.250
7.241
7.223
7.205
7.183
7.165
7.135
7.117
7.057
7.039
6.986
6.967
6.964
5.964
5.956
5.755
5.730
5.624
5.563
4.030
1.422
-0.000


Ph
Me
O
O
O
O
Cl

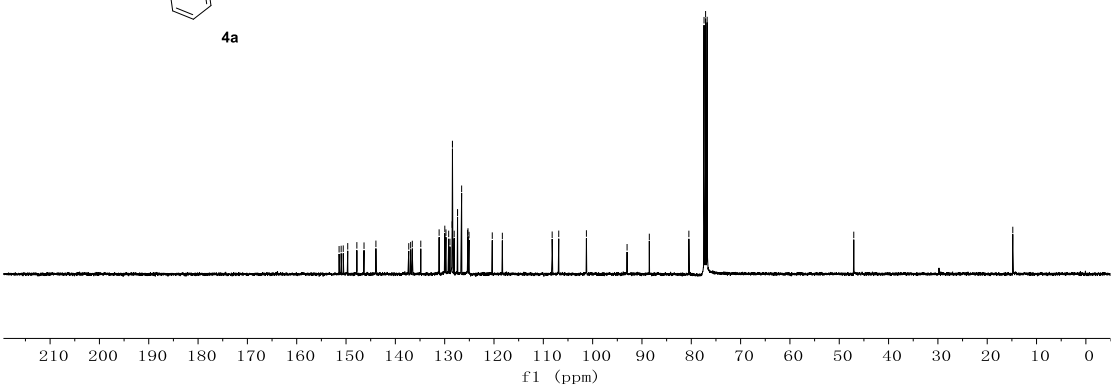
4a

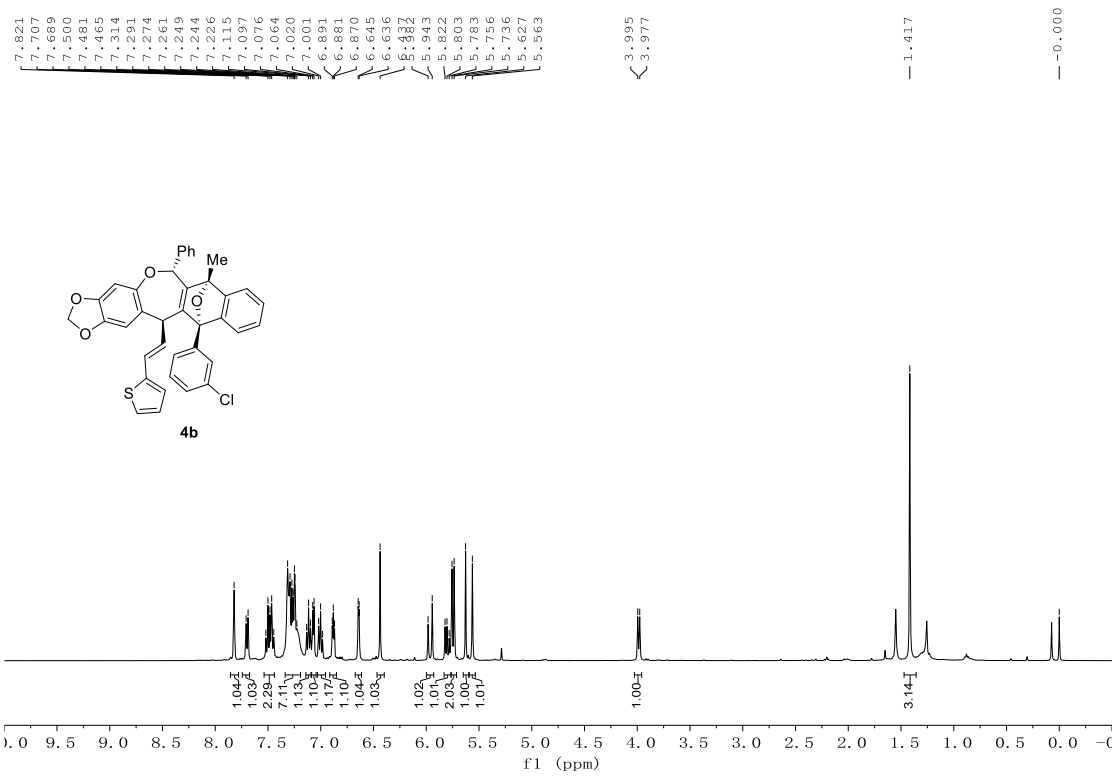

0.90
1.01
1.96
3.99
5.02
1.15
1.17
1.87
0.94
0.96
1.88
1.91
0.98
0.91
0.92
3.00
f1 (ppm)

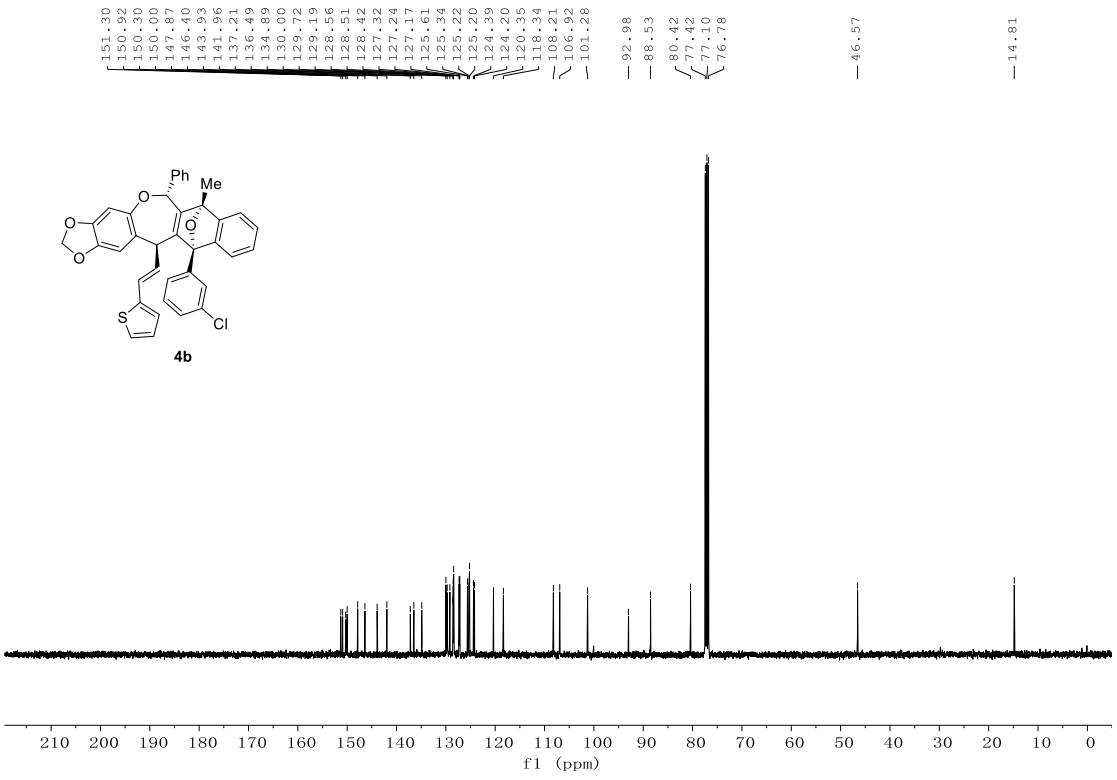

151.41
150.99
150.56
149.66
147.80
146.35
143.94
137.28
136.90
136.56
134.84
131.13
129.97
129.74
129.19
128.93
128.49
128.42
128.42
128.07
127.39
127.39
126.56
125.35
125.28
125.06
120.35
118.31
108.21
106.87
101.26
93.02
88.51
80.49
77.42
77.10
76.78
47.06
14.82

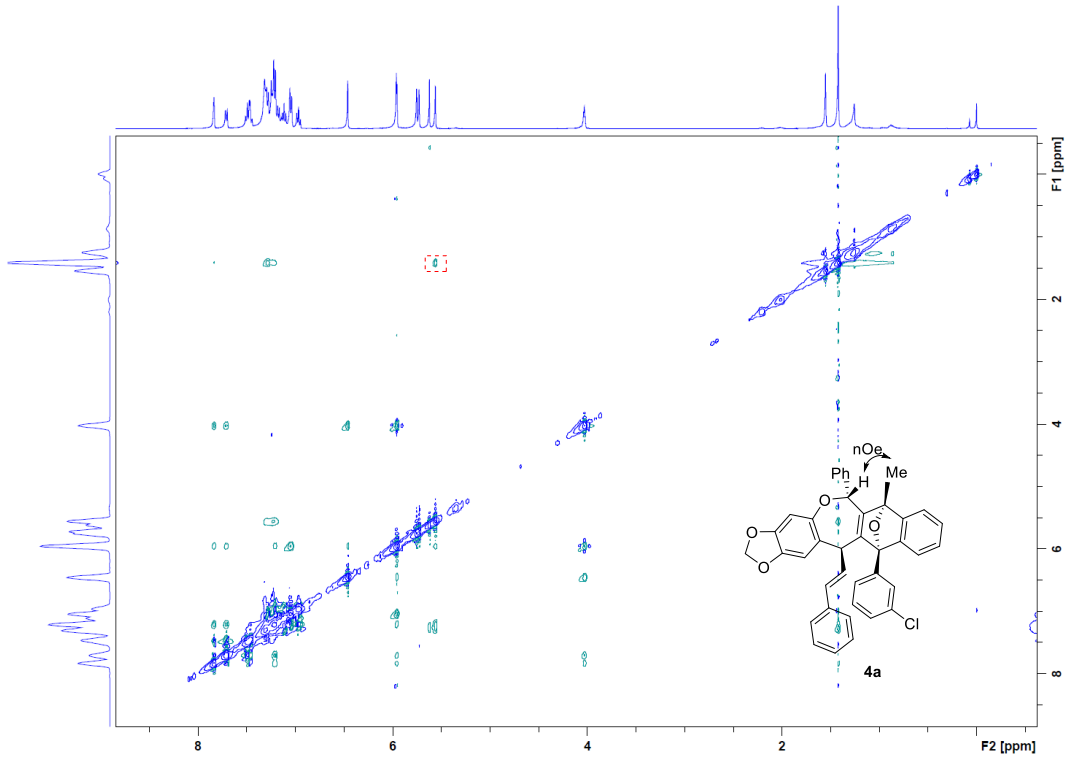

Ph
Me
O
O
O
O
Cl

4a

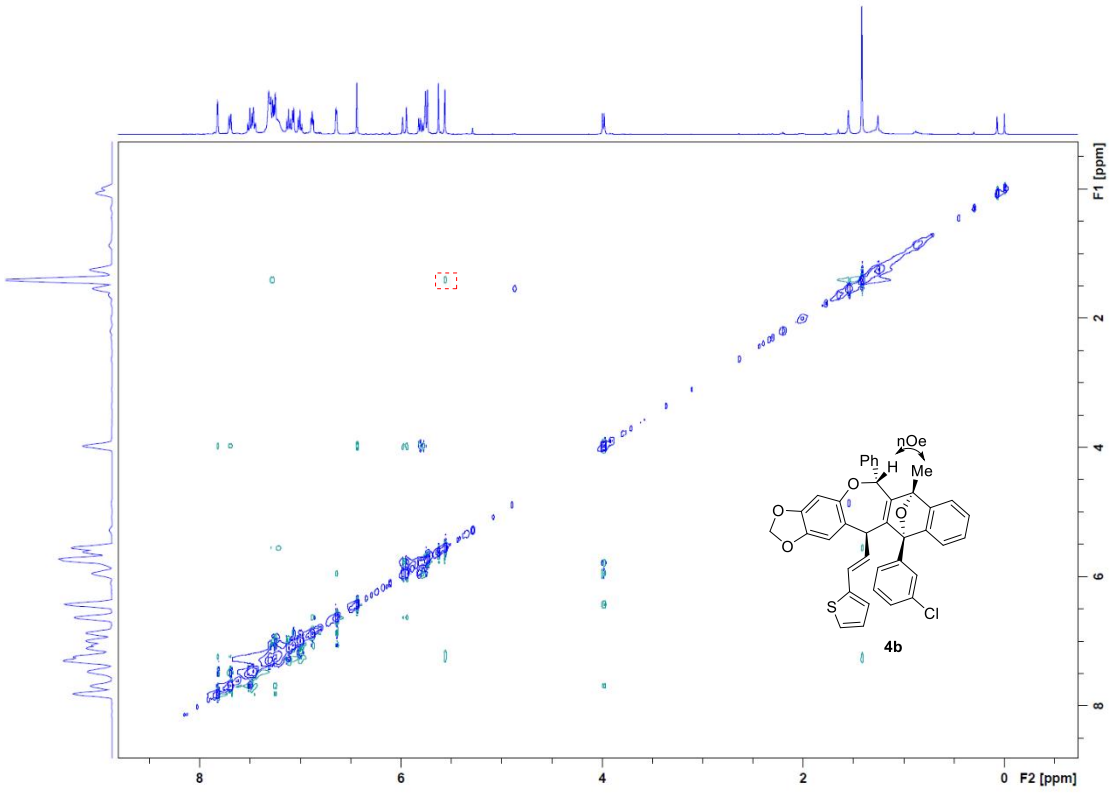

f1 (ppm)


7.821
7.707
7.689
7.500
7.481
7.465
7.314
7.291
7.274
7.261
7.249
7.244
7.226
7.115
7.097
7.076
7.064
7.020
7.001
6.891
6.881
6.870
6.645
6.636
5.943
5.822
5.803
5.783
5.756
5.736
5.627
5.563
3.995
3.977
1.417
-0.000
Ph
Me
O
O
O
O
S
Cl
4b
1.04
1.03
2.29
7.11
1.13
1.10
1.17
1.10
1.04
1.03
1.02
1.01
2.03
1.00
1.01
1.00
3.14
f1 (ppm)


151.30
150.92
150.30
150.00
147.87
146.40
143.93
141.96
137.21
136.49
134.89
130.00
129.72
129.19
128.56
128.51
128.42
127.32
127.24
127.17
125.61
125.34
125.22
125.20
124.39
124.20
120.35
118.34
108.21
106.92
101.28
92.98
88.53
80.42
77.42
77.10
76.78
46.57
14.81
Ph
Me
O
O
O
O
S
Cl
4b
f1 (ppm)

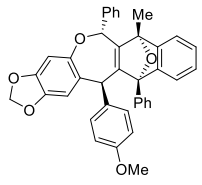


NOESY spectrum of **4a** in $CDCl_3$

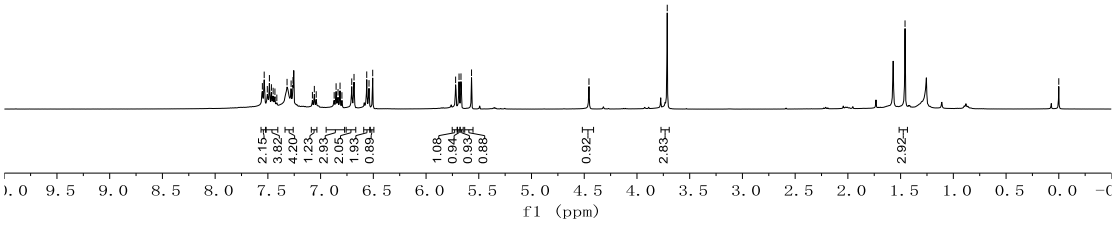


NOESY spectrum of **4b** in $CDCl_3$


7.552
7.535
7.505
7.485
7.466
7.450
7.433
7.415
7.318
7.280
7.262
7.078
7.059
7.041
6.871
6.853
6.835
6.816
6.798
6.705
6.683
6.563
6.541
6.506
5.720
5.687
5.669
5.569
4.455
3.713
1.458
-0.000


Ph
Me
O
O
O
O
Ph
OMe

5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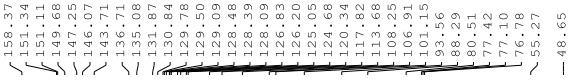
3.82
4.20
1.23
2.93
2.05
1.93
0.89
1.08
0.94
0.93
0.88
0.92
2.83
2.92
f1 (ppm)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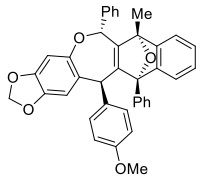
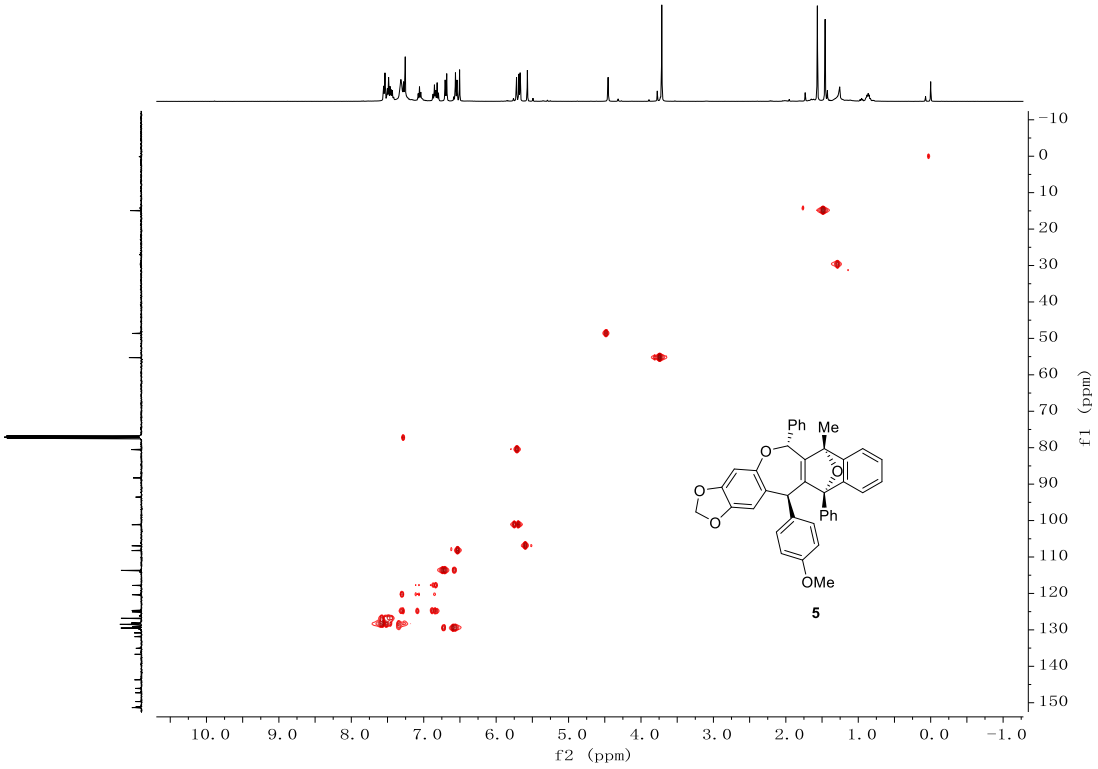
151.34
151.11
149.68
147.25
146.07
143.71
136.71
135.08
131.87
130.84
129.78
129.50
129.09
128.48
128.39
128.09
126.83
126.20
125.05
124.68
120.34
117.82
113.68
108.25
106.91
101.15
93.56
88.29
80.51
77.42
77.10
76.78
55.27
48.65
14.92

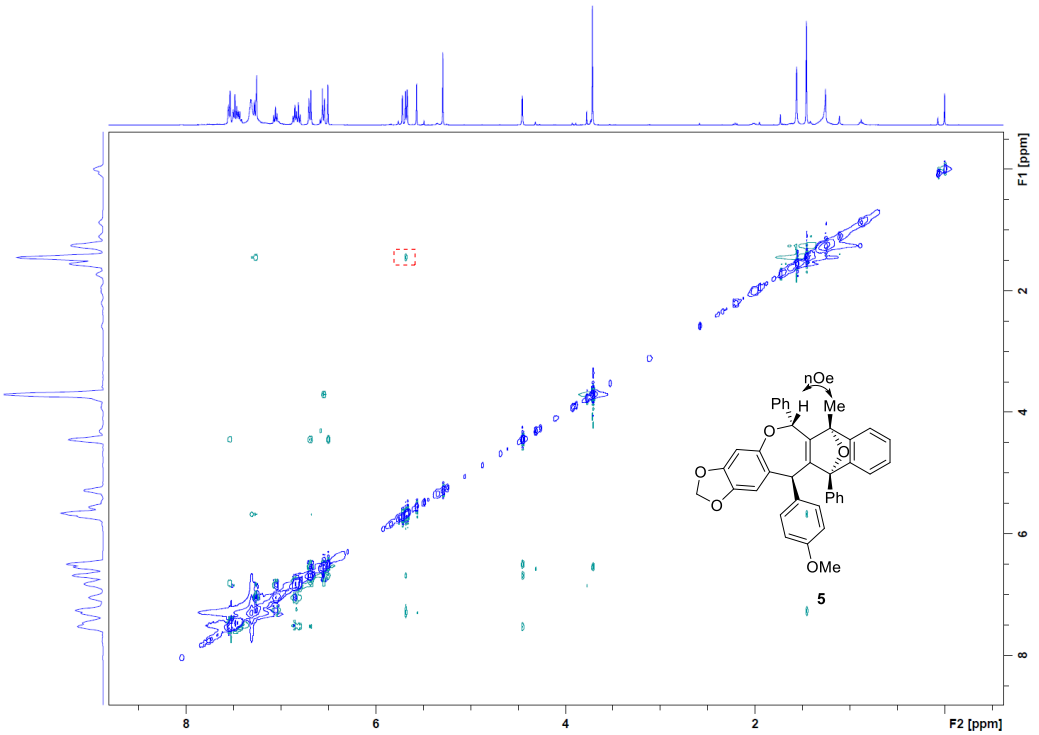

Ph
Me
O
O
O
O
Ph
OMe

5

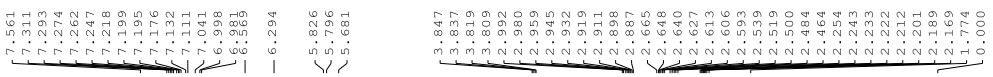
f1 (ppm)



HSQC spectrum of **5** in $CDCl_3$



NOESY spectrum of **5** in $CDCl_3$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7.247
7.218
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7.176
7.132
7.111
7.041
6.998
6.981
6.969
6.294
5.826
5.796
5.681
3.847
3.837
3.819
3.809
2.992
2.980
2.959
2.945
2.932
2.919
2.911
2.898
2.887
2.665
2.648
2.640
2.627
2.613
2.606
2.593
2.539
2.519
2.500
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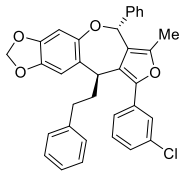
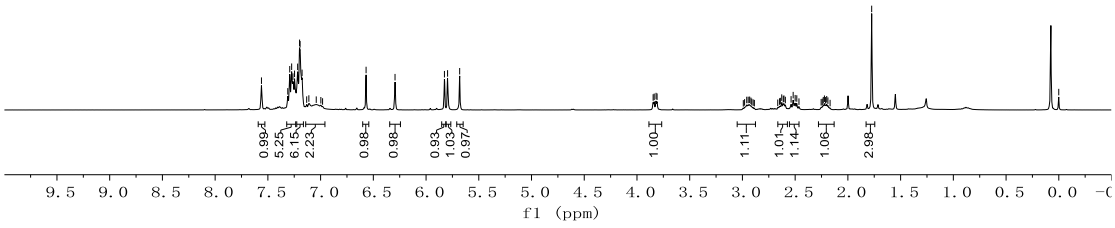
2.212
2.201
2.189
2.169
1.774
0.000


Ph
Me
O
O
O
O
Cl

6a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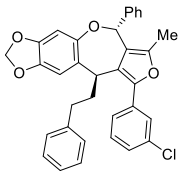
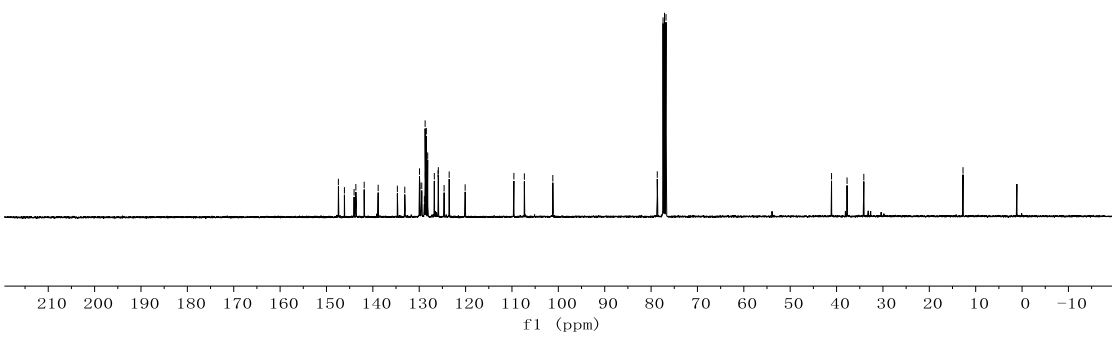
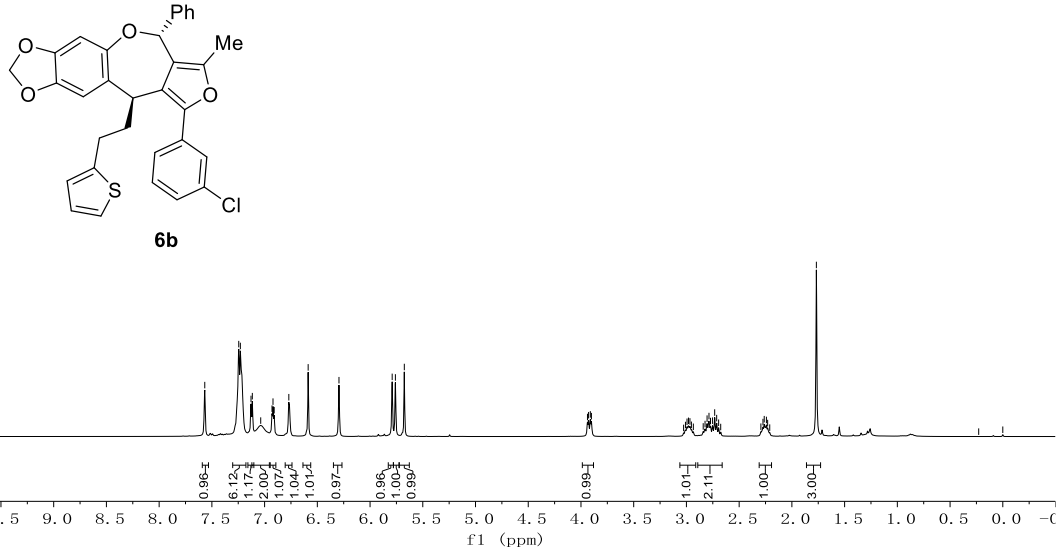
6.15
2.23
0.98
0.98
0.93
1.03
0.97
1.00
1.11
1.01
1.14
1.06
2.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


147.43
146.13
144.04
143.66
141.87
138.85
134.71
133.12
129.94
129.84
129.45
128.89
128.73
128.68
128.46
128.17
126.74
125.93
125.88
124.63
123.54
120.10
109.59
107.33
101.19
78.66
77.42
77.10
76.78
41.08
37.74
34.12
12.73


Ph
Me
O
O
O
O
Cl

6a


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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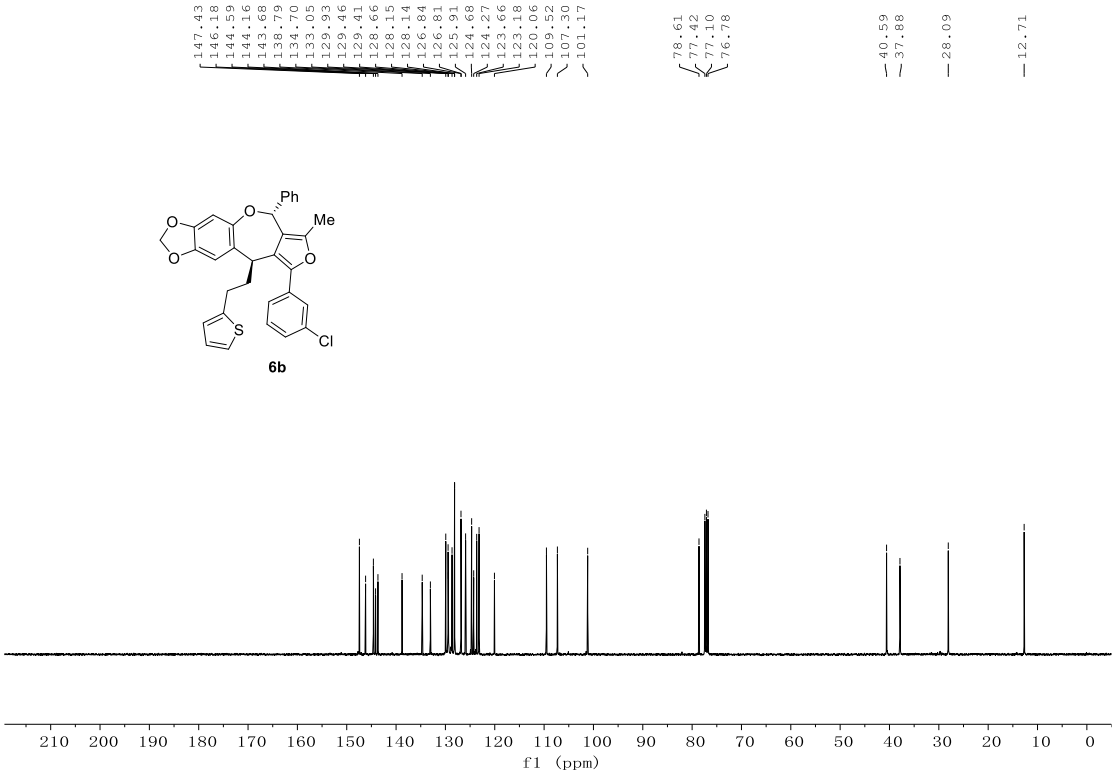
7.129
7.116
7.037
6.930
6.920
6.909
6.770
6.587
6.295
5.790
5.760
5.675
3.938
3.928
3.911
3.901
3.027
3.009
2.994
2.981
2.967
2.953
2.934
2.841
2.823
2.804
2.786
2.772
2.752
2.732
2.713
2.695
2.675
2.294
2.274
2.262
2.241
2.230
2.210
1.768
0.229
-0.000
Ph
Me
O
O
O
O
S
Cl
6b
0.96
6.12
1.17
2.00
1.07
1.04
1.01
0.97
0.96
1.00
0.99
0.99
1.01
2.11
1.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


147.43
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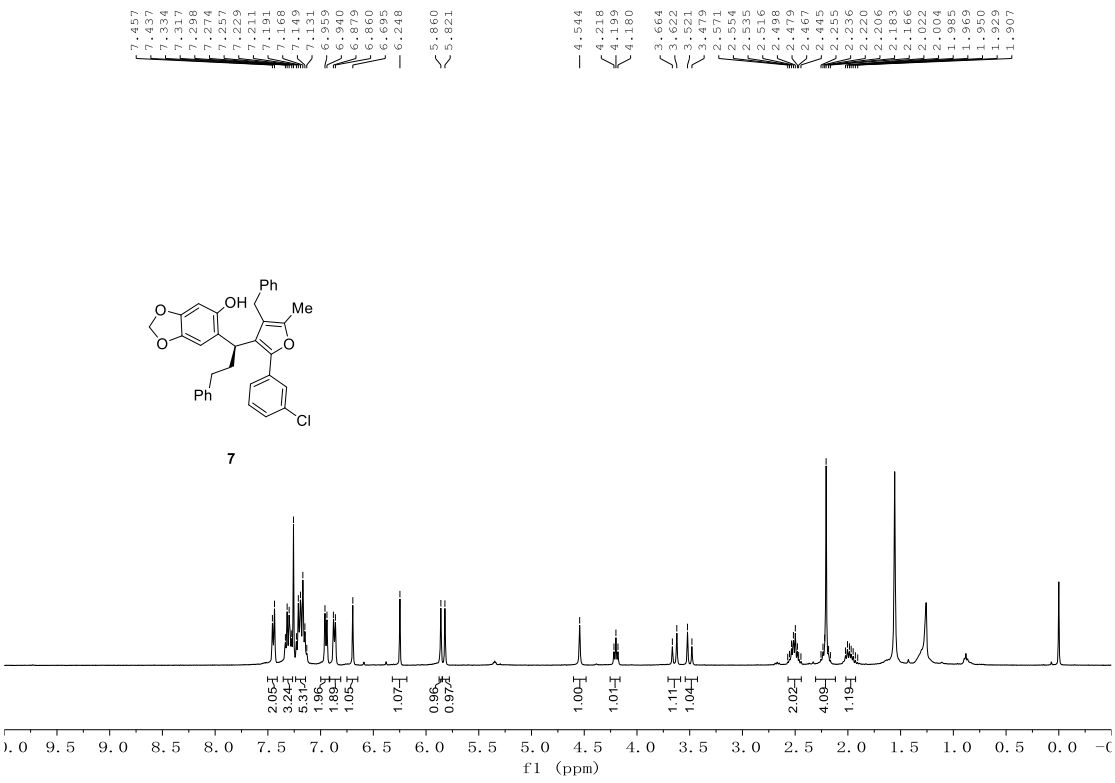
144.16
143.68
138.79
134.70
133.05
129.93
129.46
129.41
128.66
128.15
128.14
126.84
126.81
125.91
124.68
124.27
123.66
123.18
120.06
109.52
107.30
101.17
78.61
77.42
77.10
76.78
40.59
37.88
28.09
12.71
Ph
Me
O
O
O
O
S
Cl
6b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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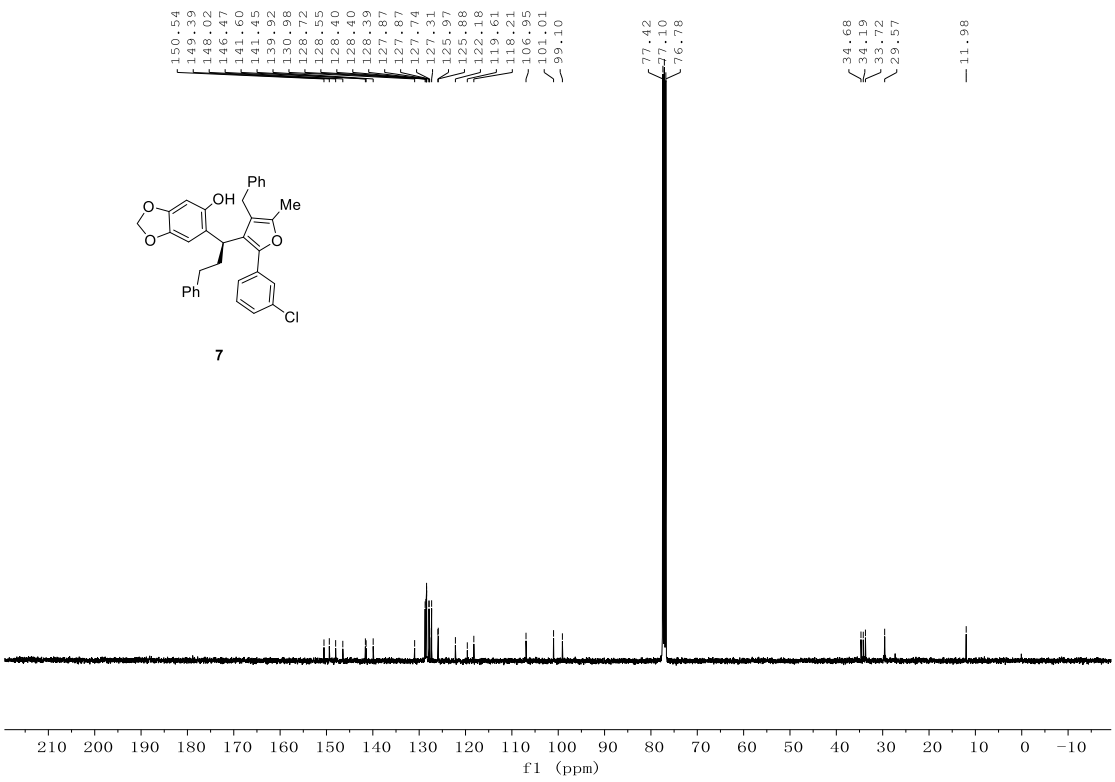
7.191
7.168
7.149
7.131
6.959
6.940
6.879
6.860
6.695
6.248
5.860
5.821
4.544
4.218
4.199
4.180
3.664
3.622
3.621
3.479
2.571
2.554
2.535
2.516
2.498
2.479
2.467
2.445
2.255
2.236
2.220
2.206
2.183
2.166
2.022
2.004
1.985
1.969
1.950
1.929
1.907
OH
Ph
Me
O
O
O
Ph
Cl
7
2.05
3.24
5.31
1.96
1.89
1.05
1.07
0.96
0.97
1.00
1.01
1.11
1.04
2.02
4.09
1.19
f1 (ppm)


150.54
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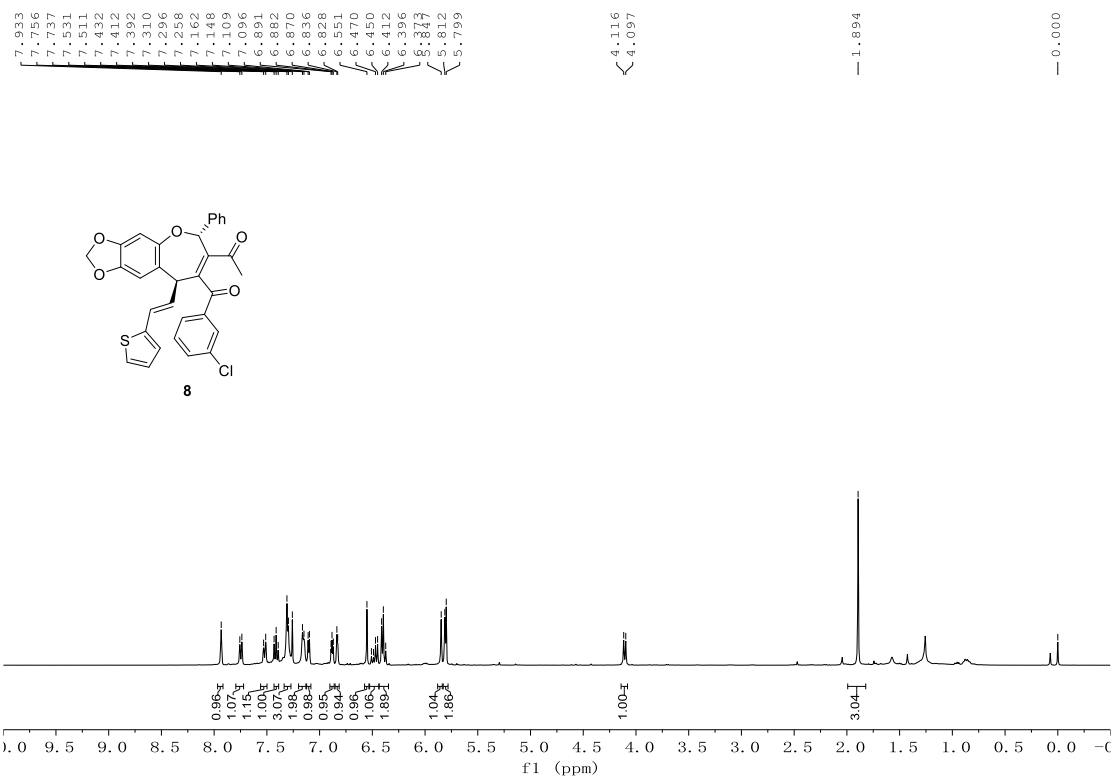
146.47
141.60
141.45
139.92
130.98
128.72
128.55
128.40
128.40
128.39
127.87
127.87
127.74
127.31
125.97
125.88
122.18
119.61
118.21
106.95
101.01
99.10
77.42
77.10
76.78
34.68
34.19
33.72
29.57
11.98
OH
Ph
Me
O
O
O
Ph
Cl
7
f1 (ppm)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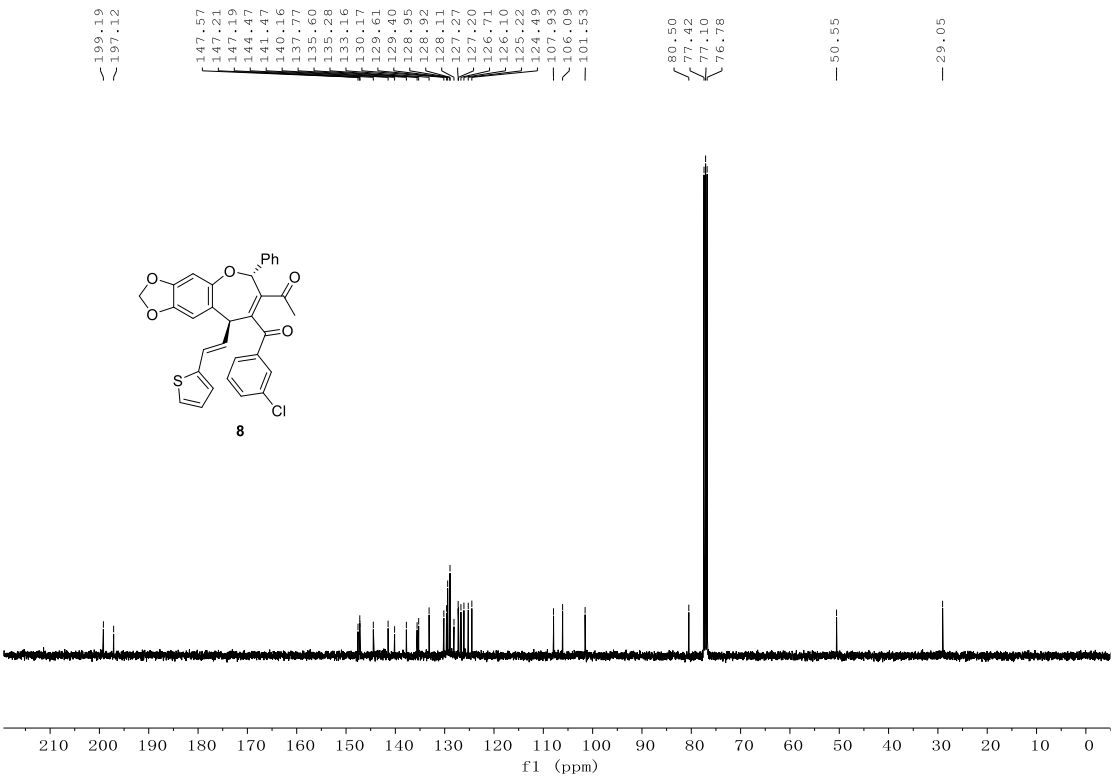
7.511
7.432
7.412
7.392
7.310
7.296
7.258
7.162
7.148
7.109
7.096
6.891
6.882
6.870
6.836
6.828
6.551
6.470
6.450
6.412
6.396
6.373
5.847
5.812
5.799
4.116
4.097
1.894
0.000
Ph
O
O
O
O
O
S
Cl
8
0.96
1.07
1.15
1.00
3.07
1.98
0.98
0.95
0.94
0.96
1.06
1.89
1.04
1.86
1.00
3.04
f1 (ppm)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197.12
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147.19
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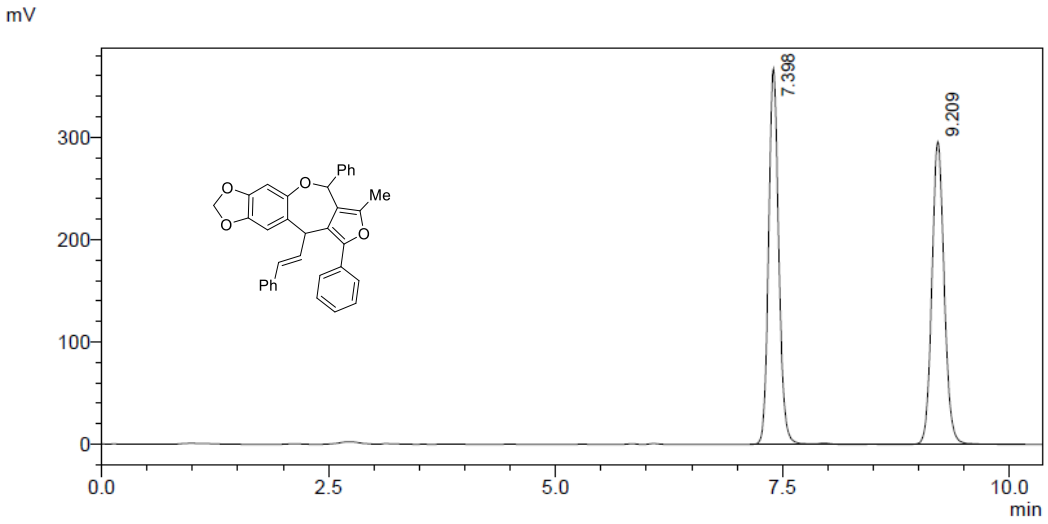
141.47
140.16
137.77
135.60
135.28
133.16
130.17
129.61
129.40
128.95
128.92
128.11
127.27
127.20
126.71
126.10
125.22
124.49
107.93
106.09
101.53
80.50
77.42
77.10
76.78
50.55
29.05
Ph
O
O
O
O
O
S
Cl
8
f1 (ppm)

8. Copies of HPLC Chromatographs.

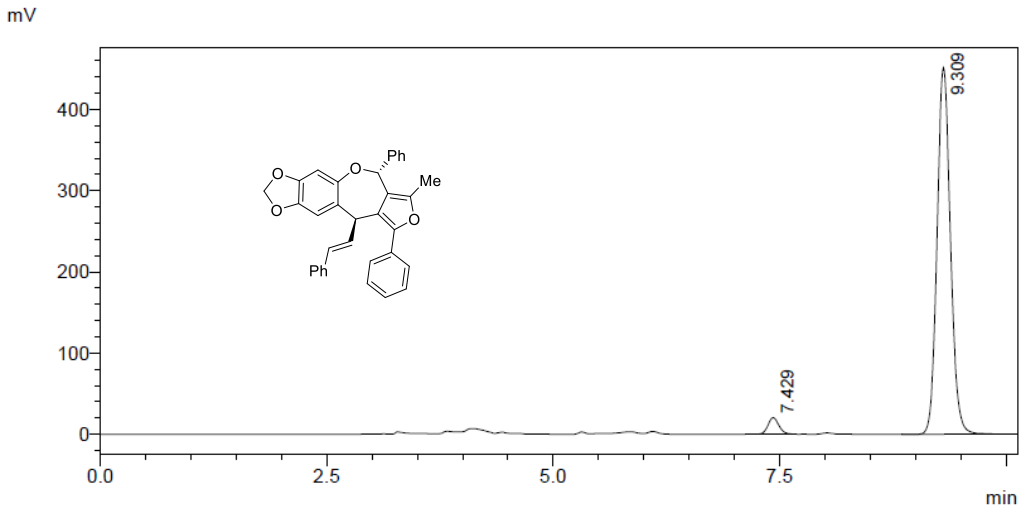
<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.398	2869463	367708	50.641
2	9.209	2796866	296133	49.359
		5666329	663841	100.000

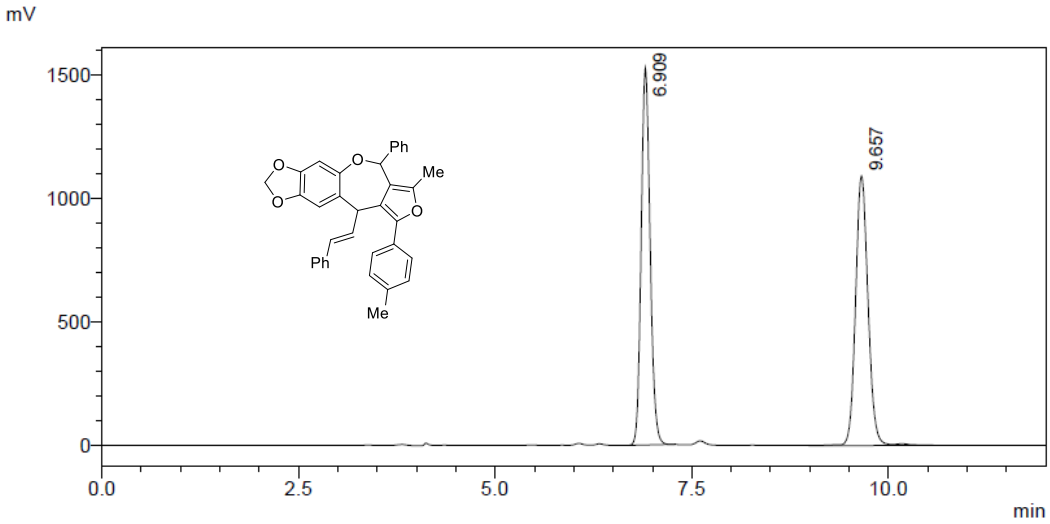
<Chromatogram>



<Peak Table>

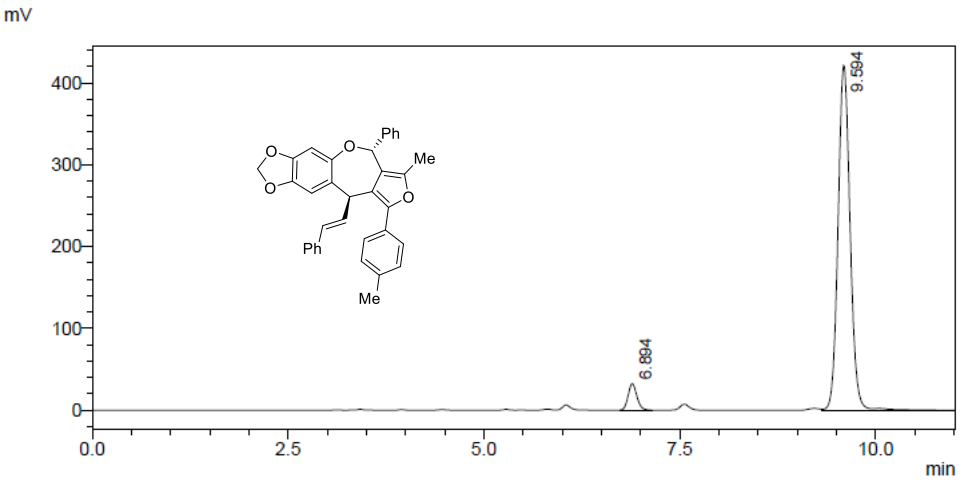
Peak#	Ret. Time	Area	Height	Area%
1	7.429	168623	20273	3.503
2	9.309	4644423	451561	96.497
		4813046	471834	100.000

<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	6.909	12068742	1524303	49.933
2	9.657	12101174	1090499	50.067
		24169916	2614802	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	6.894	249470	32358	5.229
2	9.594	4521452	421547	94.771
		4770921	453905	100.000

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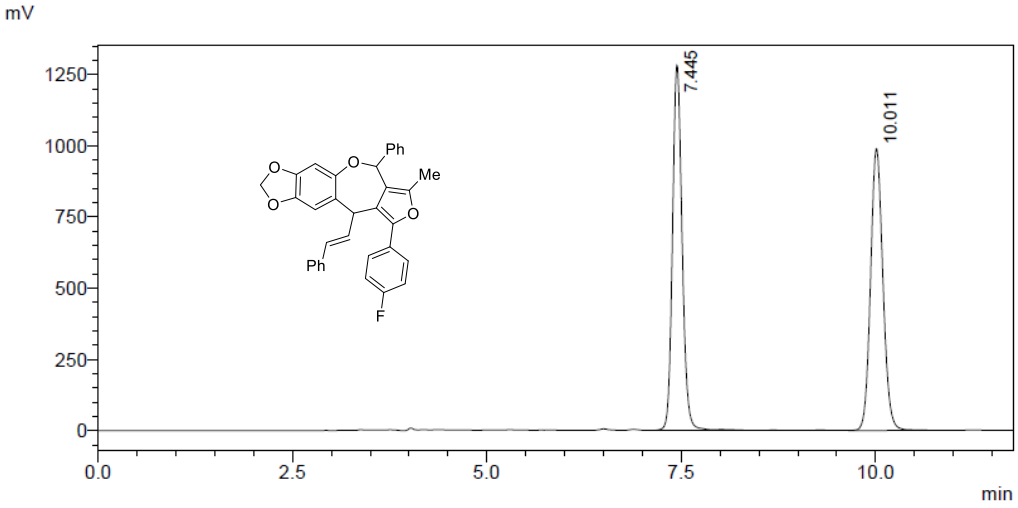

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.445	11179122	1283301	50.534
2	10.011	10942974	989772	49.466
		22122096	2273073	100.000

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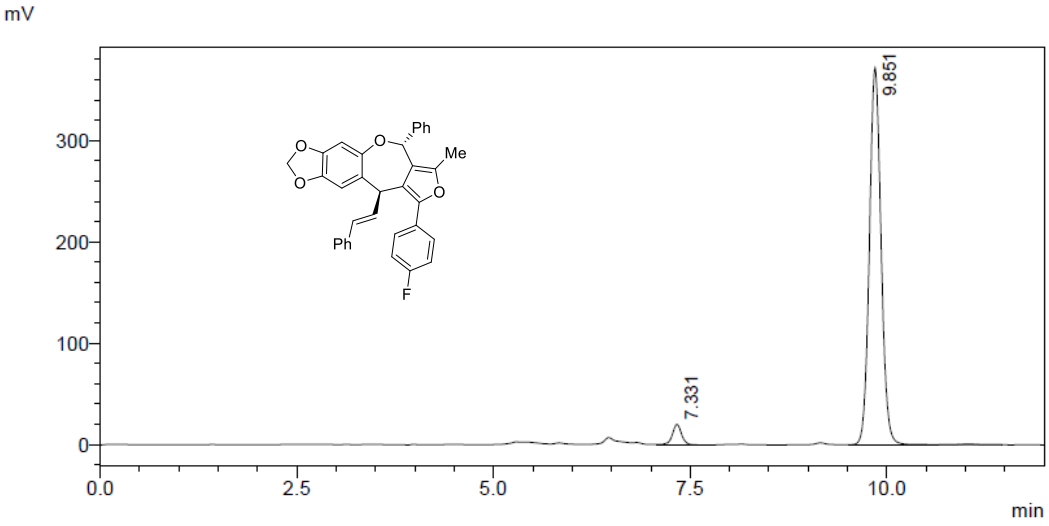

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.331	170457	20269	4.225
2	9.851	3863770	372242	95.775
		4034227	392511	100.000

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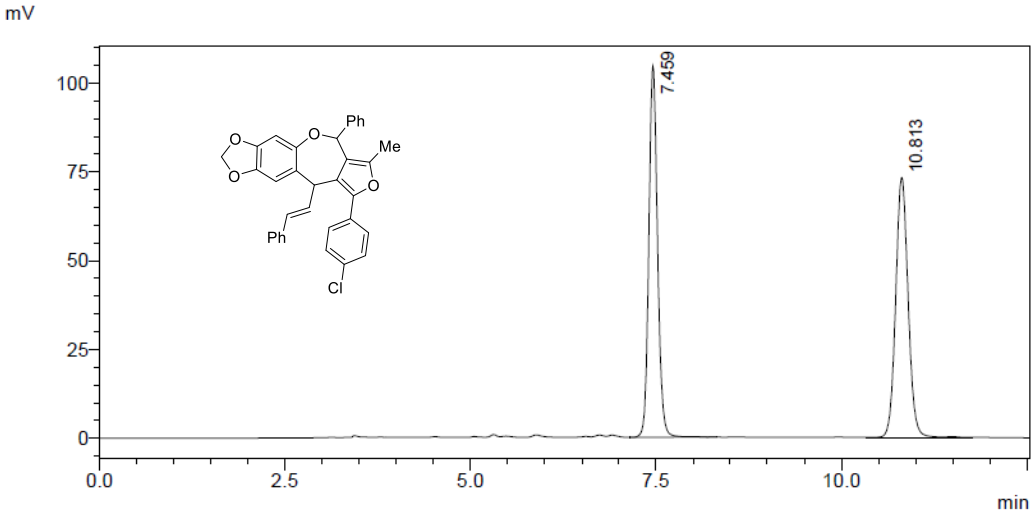

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.459	856777	104506	50.054
2	10.813	854932	73213	49.946
		1711709	177718	100.000

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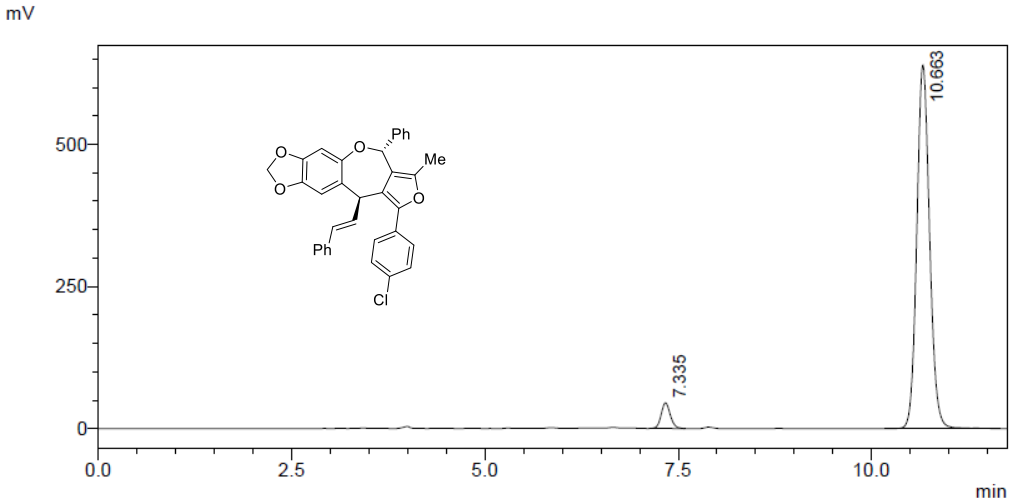

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.335	364972	44892	4.720
2	10.663	7367793	639074	95.280
		7732766	683966	100.000

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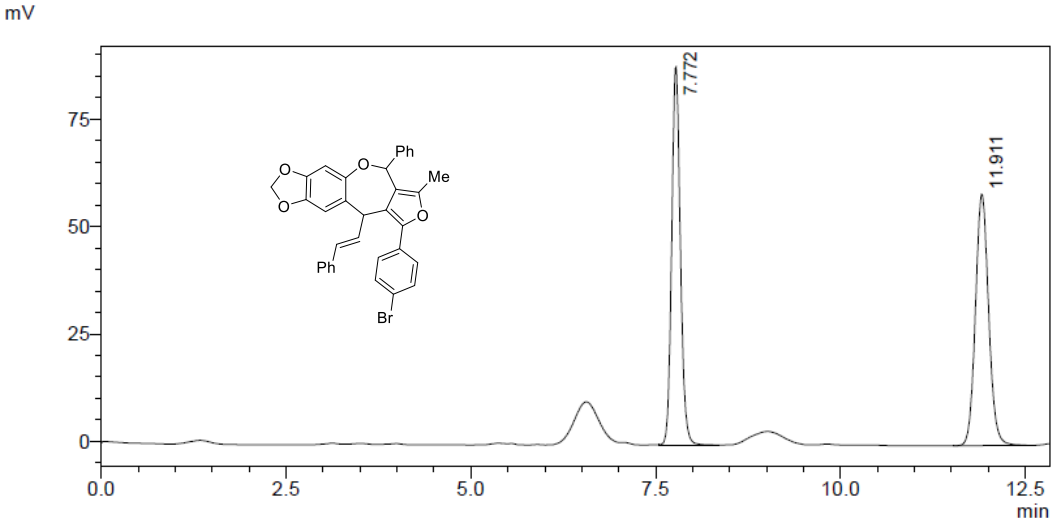

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.772	722675	88004	49.799
2	11.911	728519	58476	50.201
		1451195	146480	100.000

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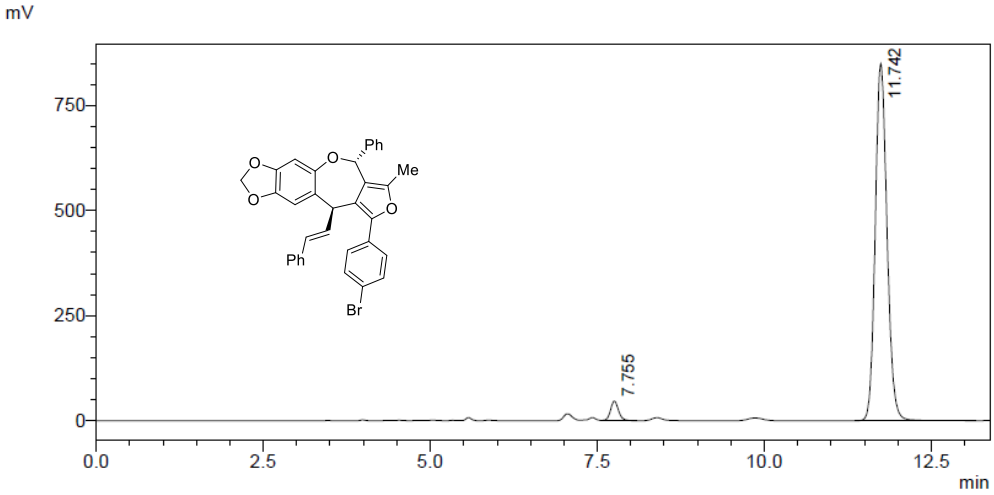

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.755	394675	46622	3.647
2	11.742	10428667	849369	96.353
		10823342	895991	100.000

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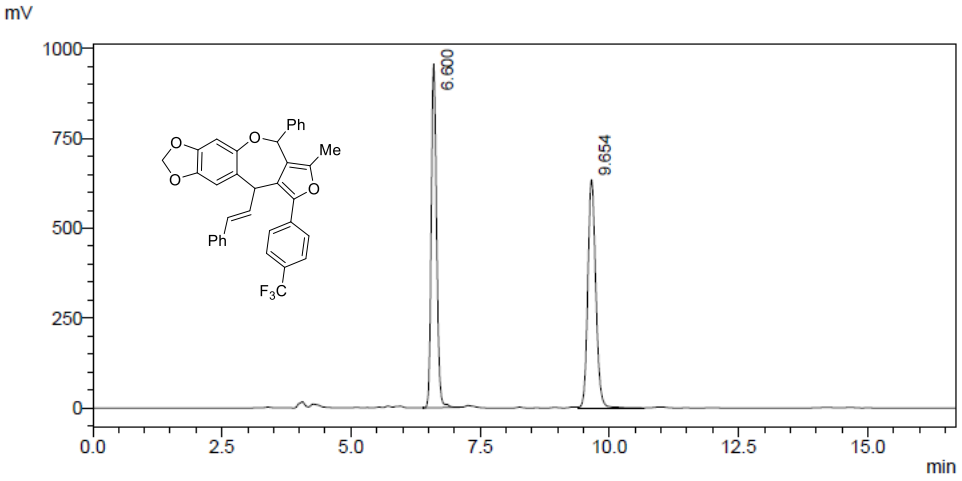

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	6.600	6845518	957900	50.020
2	9.654	6839914	634586	49.980
		13685432	1592486	100.000

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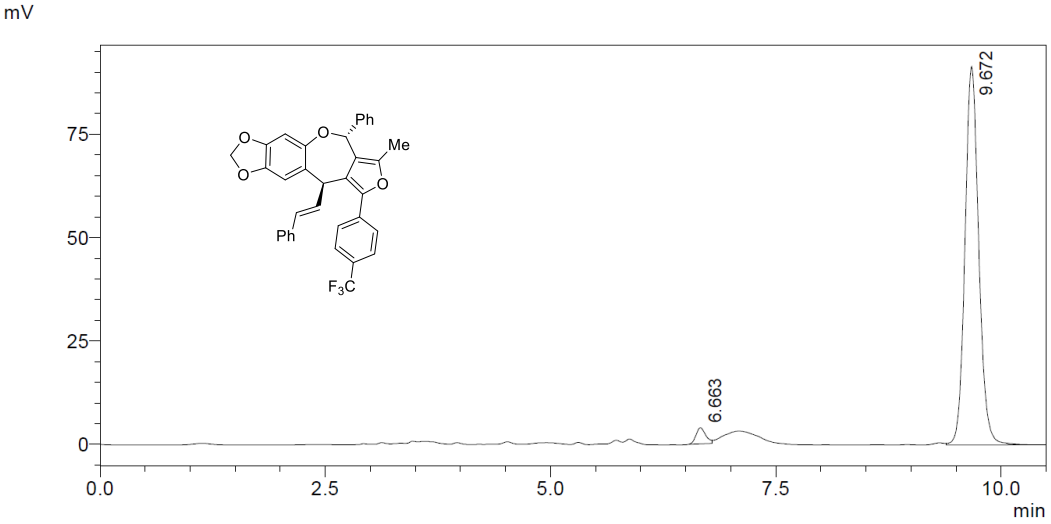

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	6.663	29100	3882	2.803
2	9.672	1009084	91551	97.197
		1038184	95433	100.000

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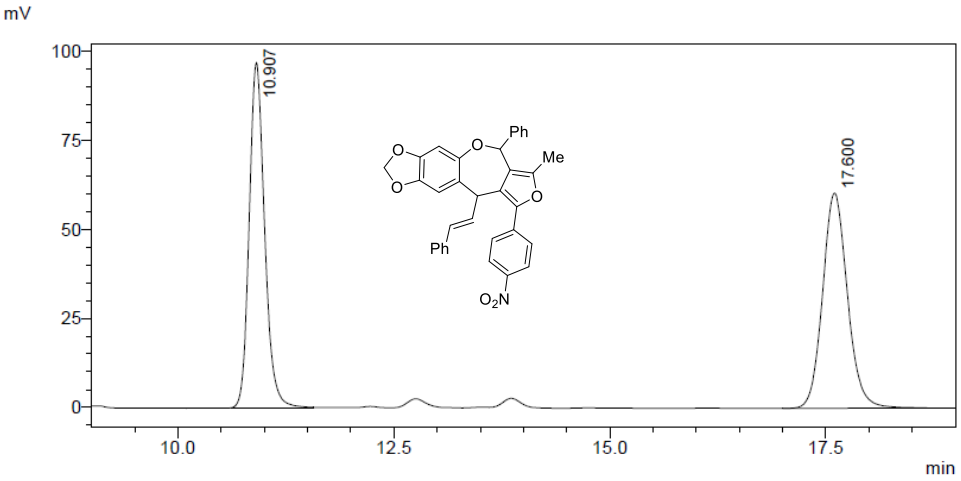

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	10.907	1206944	96921	49.885
2	17.600	1212516	60425	50.115
		2419460	157346	100.000

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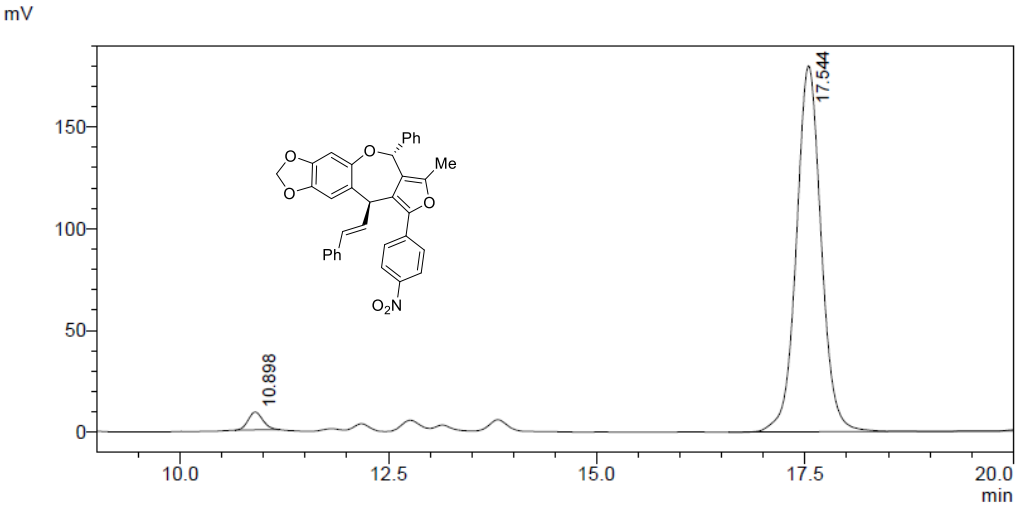

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	10.898	108151	8757	2.818
2	17.544	3730291	179953	97.182
		3838442	188709	100.000

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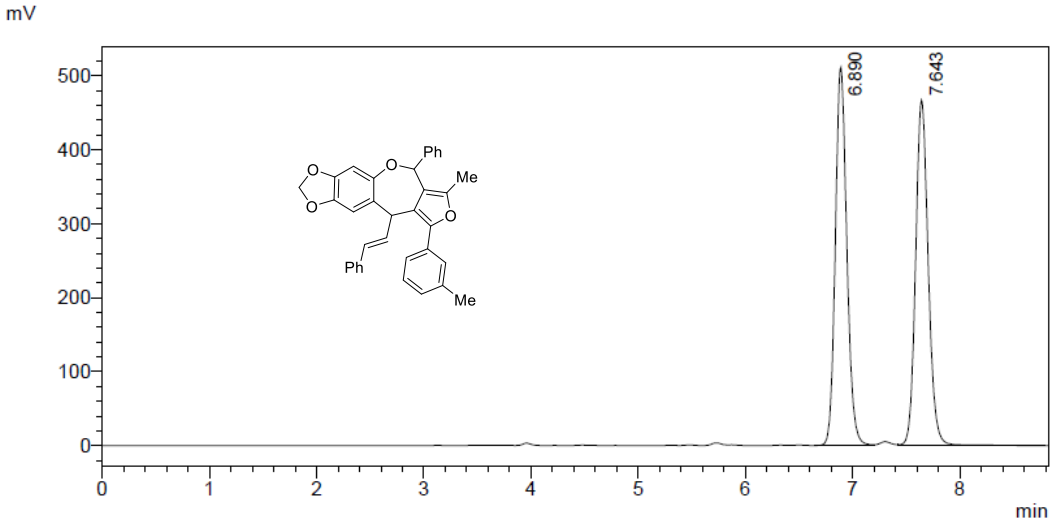
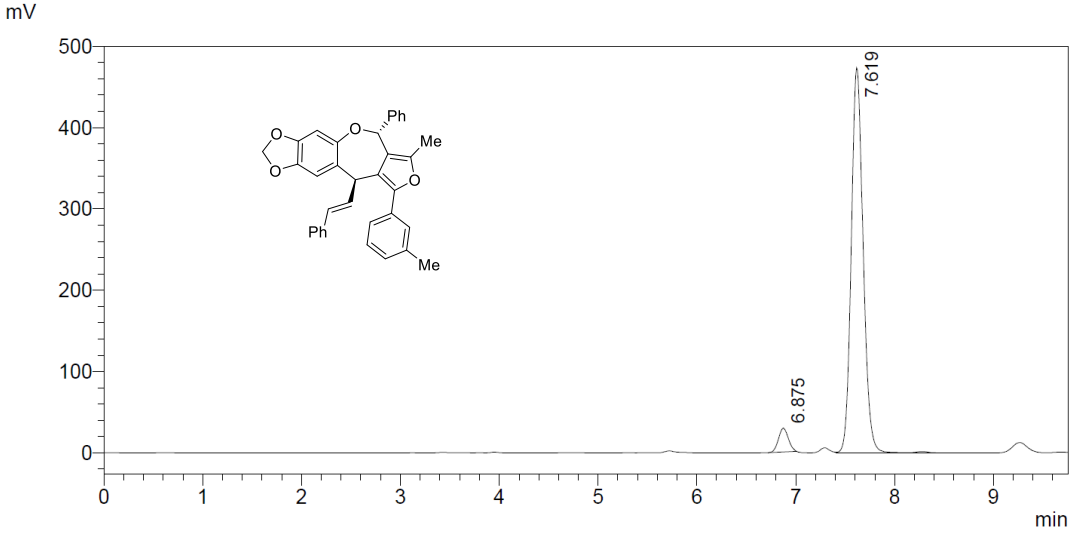


<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	6.890	3841211	511330	50.090
2	7.643	3827361	466785	49.910
		7668572	978115	100.000

<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	6.875	205088	29275	4.950
2	7.619	3938388	474071	95.050
		4143476	503346	100.000

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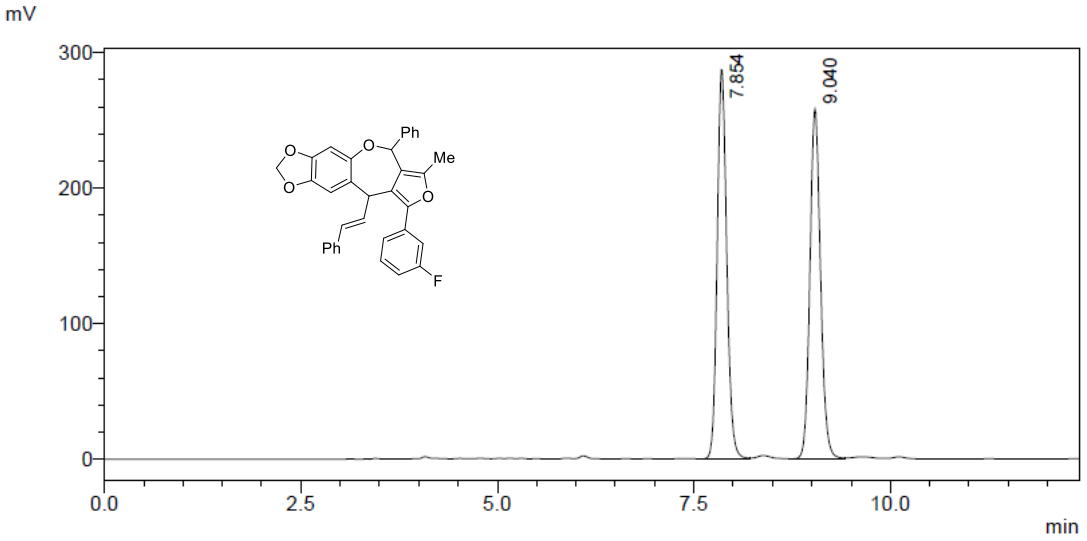
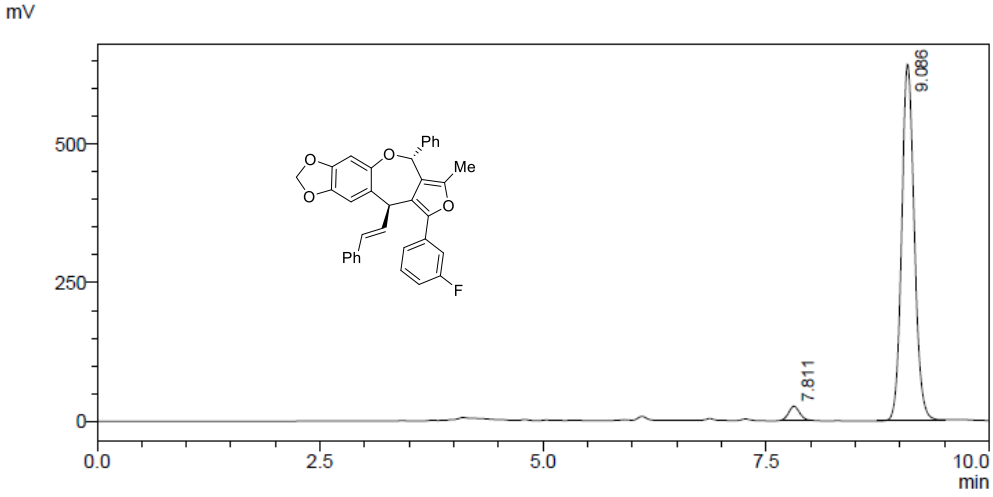


<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.854	2437640	287518	49.989
2	9.040	2438672	258161	50.011
		4876312	545679	100.000

<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.811	223328	25954	3.383
2	9.086	6378278	644327	96.617
		6601606	670281	100.000

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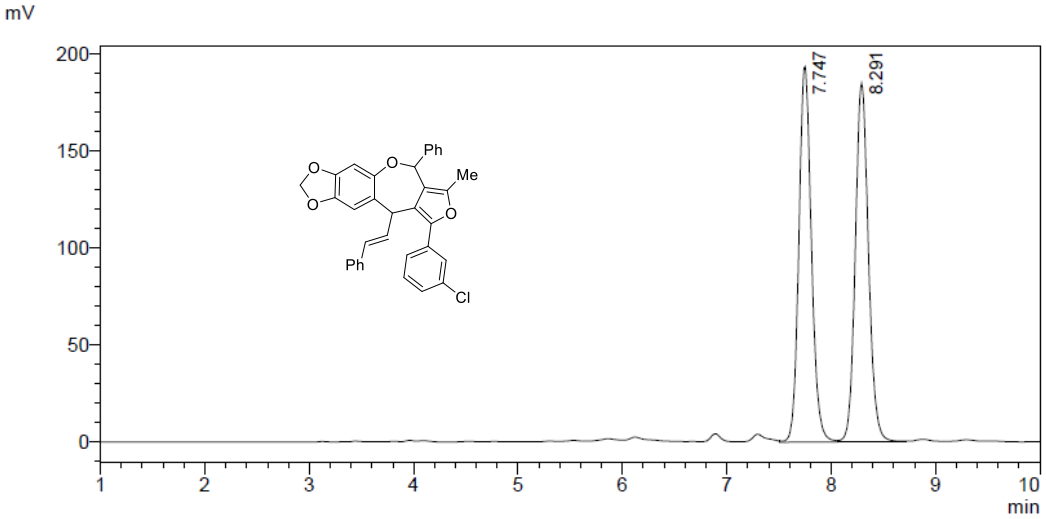
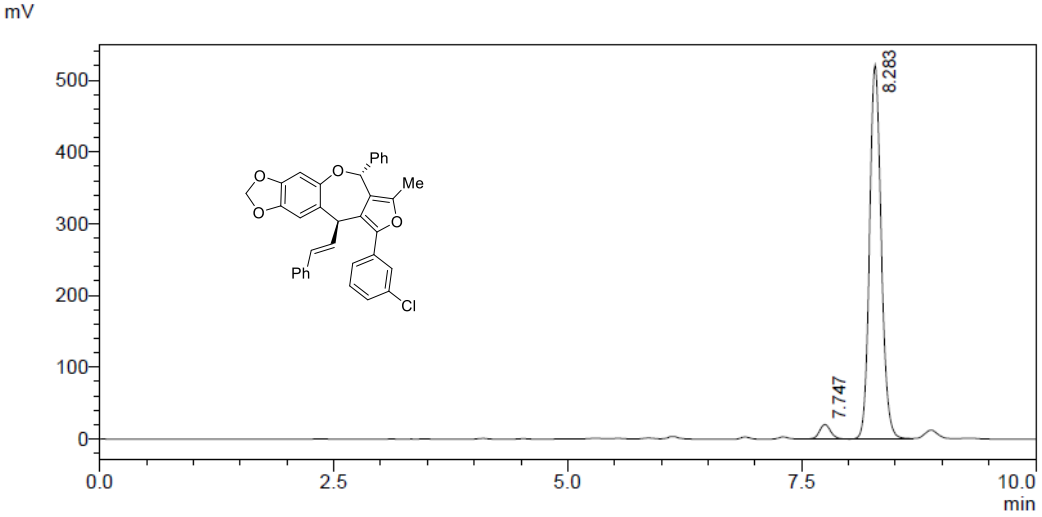


<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.747	1619090	193658	49.871
2	8.291	1627447	185043	50.129
		3246537	378701	100.000

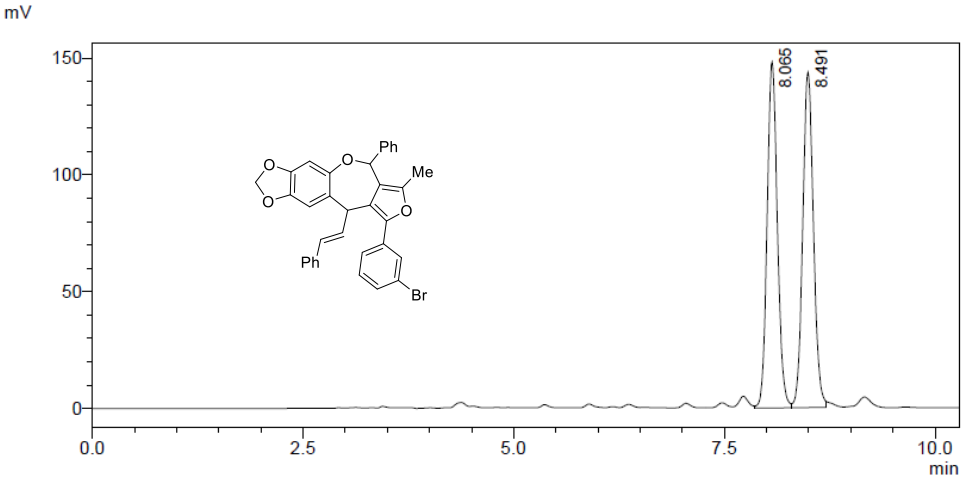
<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.747	176723	20519	3.738
2	8.283	4551166	521716	96.262
		4727889	542234	100.000

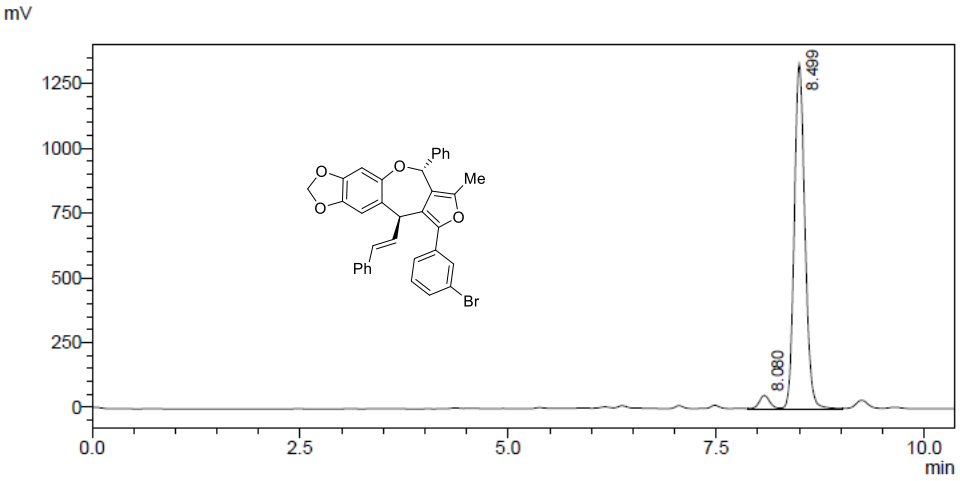
<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	8.065	1250873	148079	49.605
2	8.491	1270785	143513	50.395
		2521658	291592	100.000

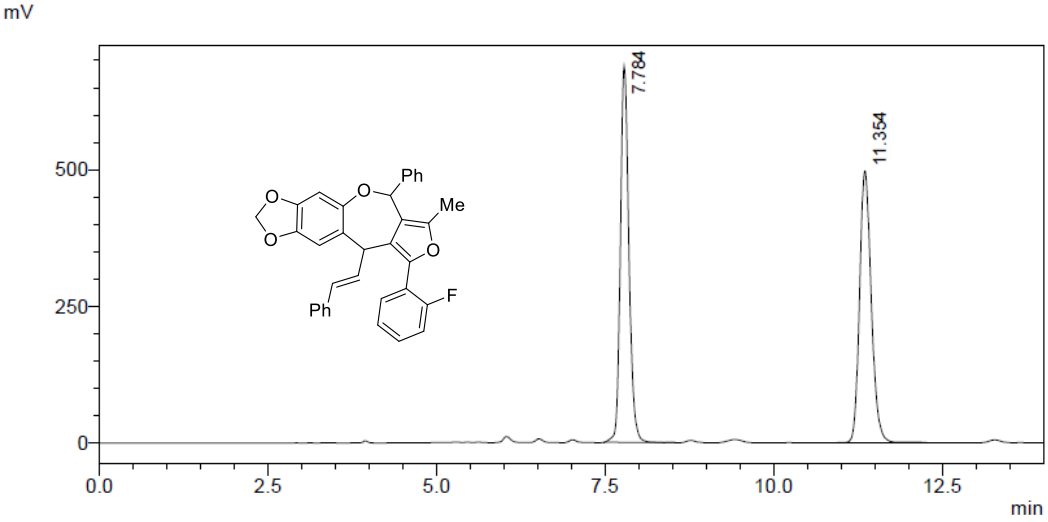
<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	8.080	453452	51730	3.674
2	8.499	11887947	1331899	96.326
		12341399	1383628	100.000

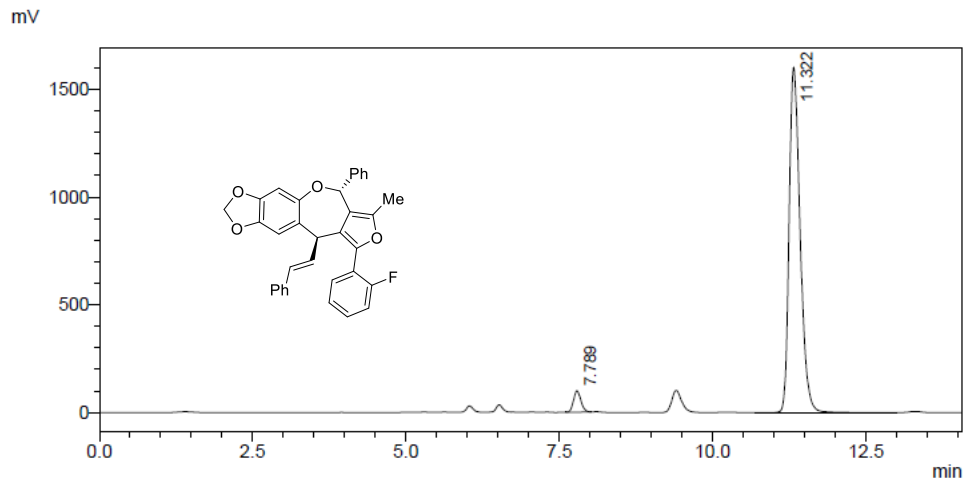
<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.784	6057953	688430	50.100
2	11.354	6033822	497007	49.900
		12091775	1185437	100.000

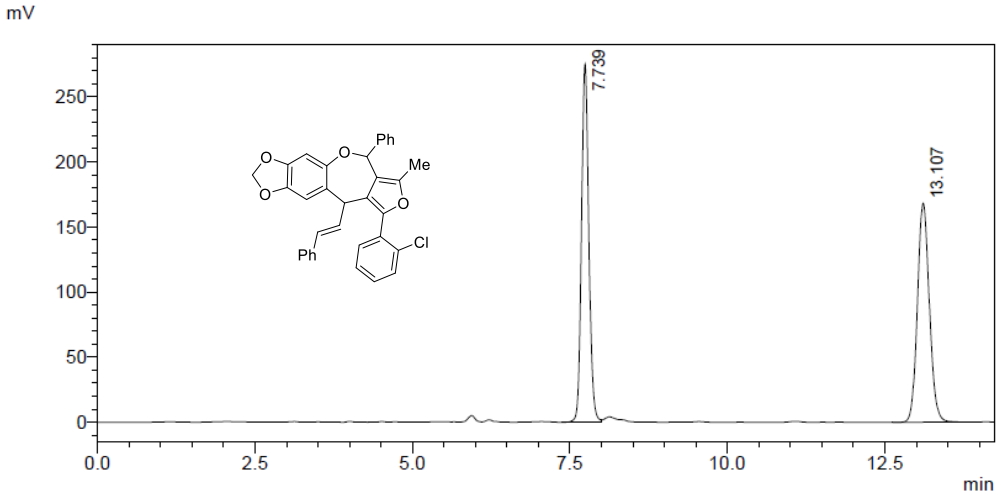
<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.789	832117	98885	4.006
2	11.322	19941670	1601472	95.994
		20773787	1700357	100.000

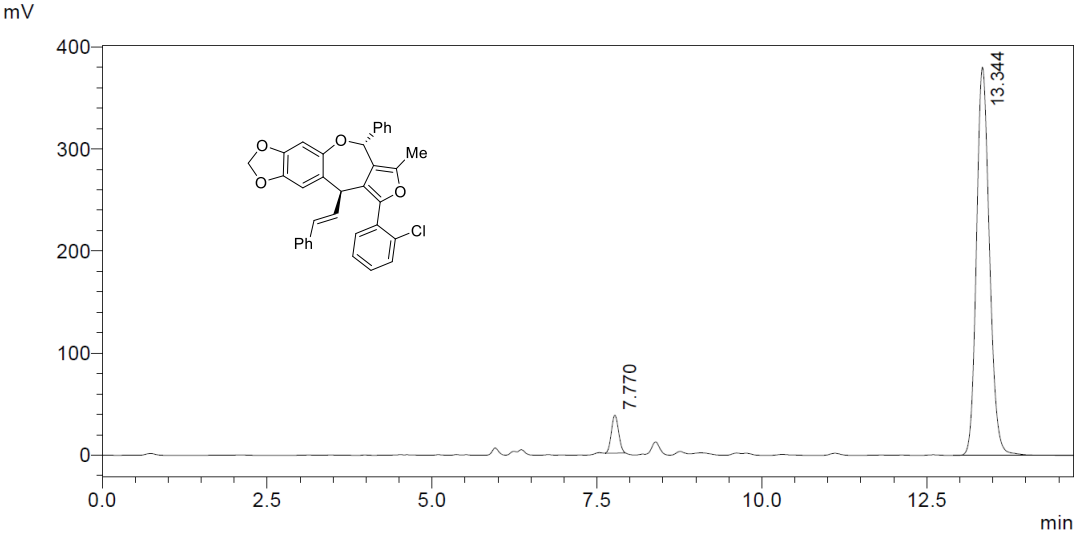
<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.739	2230541	275125	50.126
2	13.107	2219362	168190	49.874
		4449903	443314	100.000

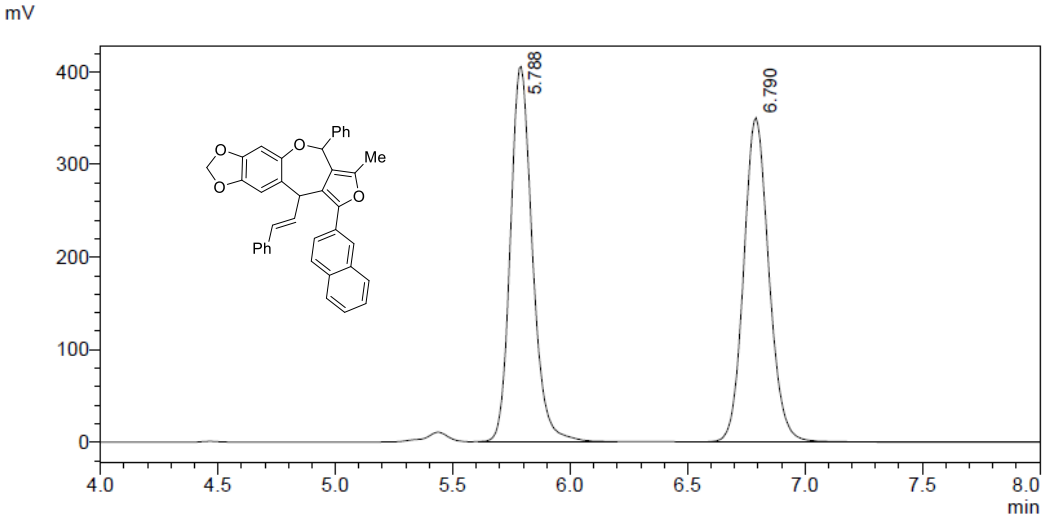
<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.770	283626	37201	5.155
2	13.344	5218163	380221	94.845
		5501789	417422	100.000

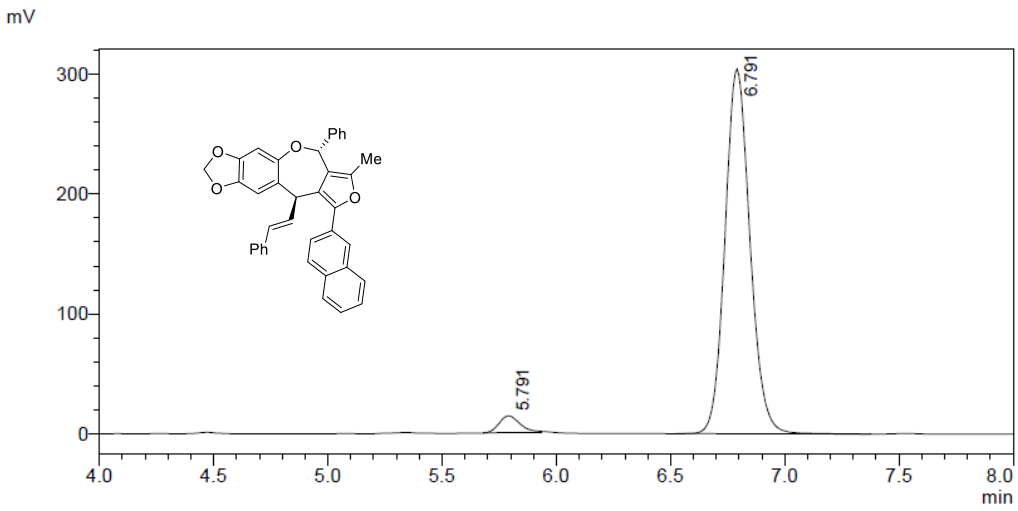
<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.788	2637999	405280	50.100
2	6.790	2627495	350419	49.900
		5265494	755699	100.000

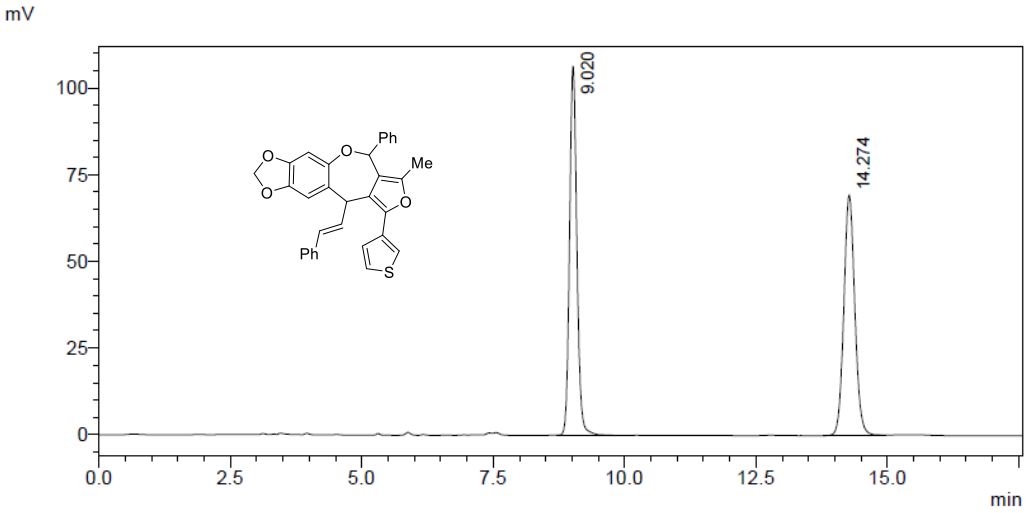
<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.791	89997	13985	3.740
2	6.791	2316513	304636	96.260
		2406510	318620	100.000

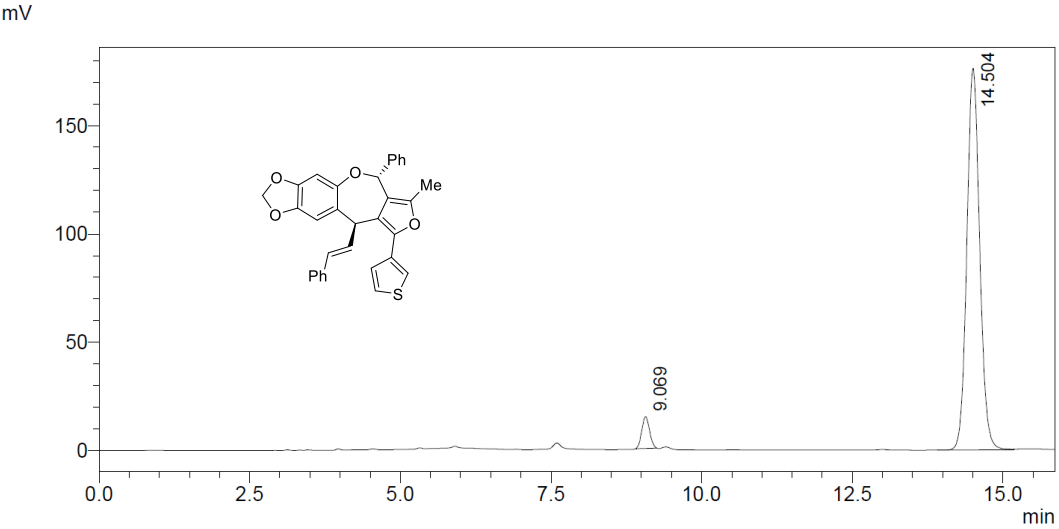
<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	9.020	1028822	106372	50.394
2	14.274	1012720	69396	49.606
		2041542	175768	100.000

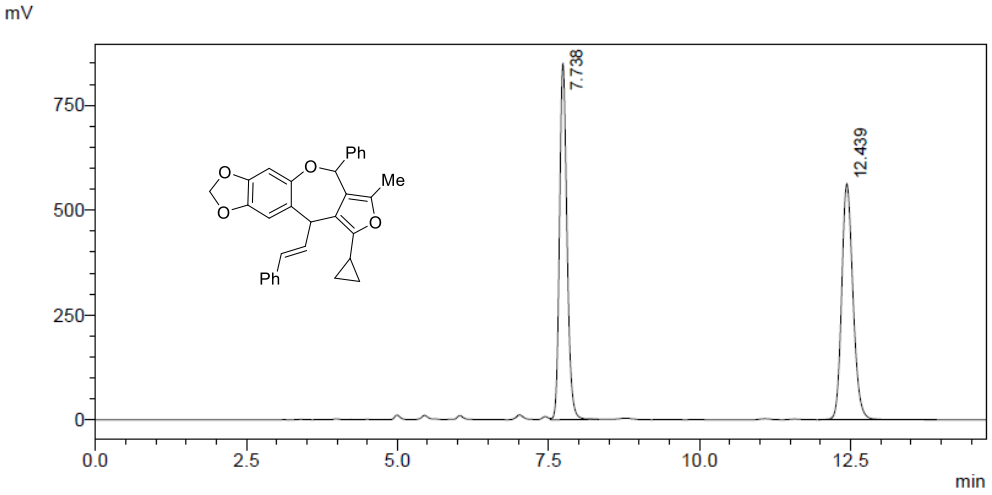
<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	9.069	132648	14717	4.823
2	14.504	2617471	176111	95.177
		2750119	190828	100.000

<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.738	7321574	848735	50.016
2	12.439	7316970	562191	49.984
		14638544	1410926	100.000

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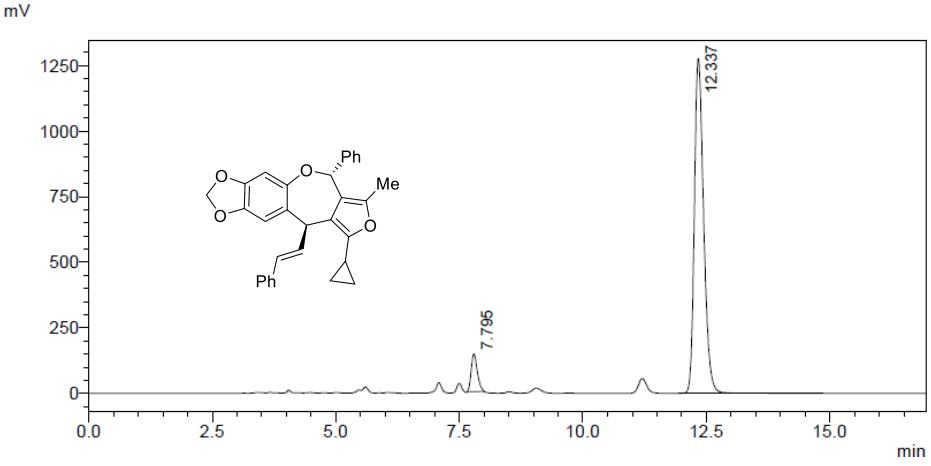

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.795	1252278	144274	6.957
2	12.337	16747245	1276360	93.043
		17999524	1420634	100.000

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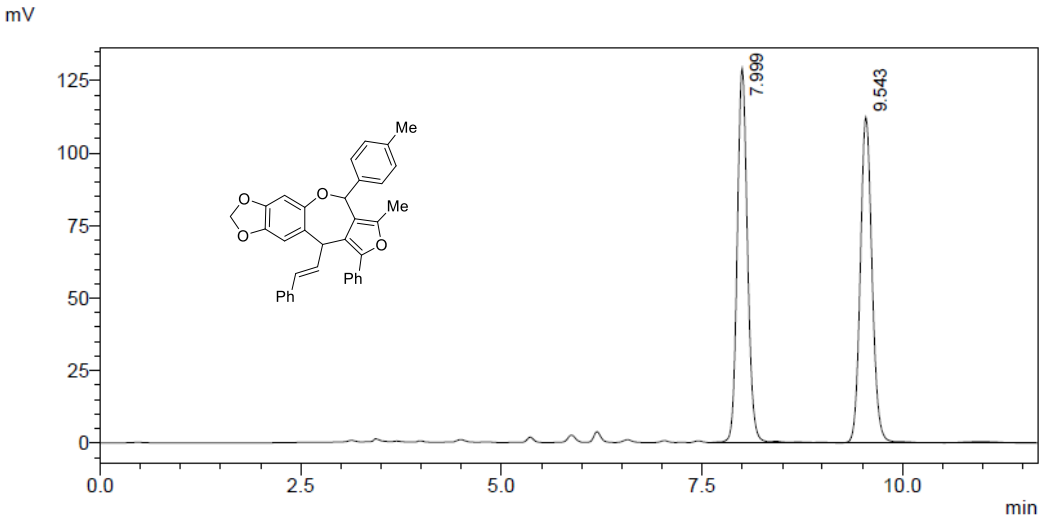
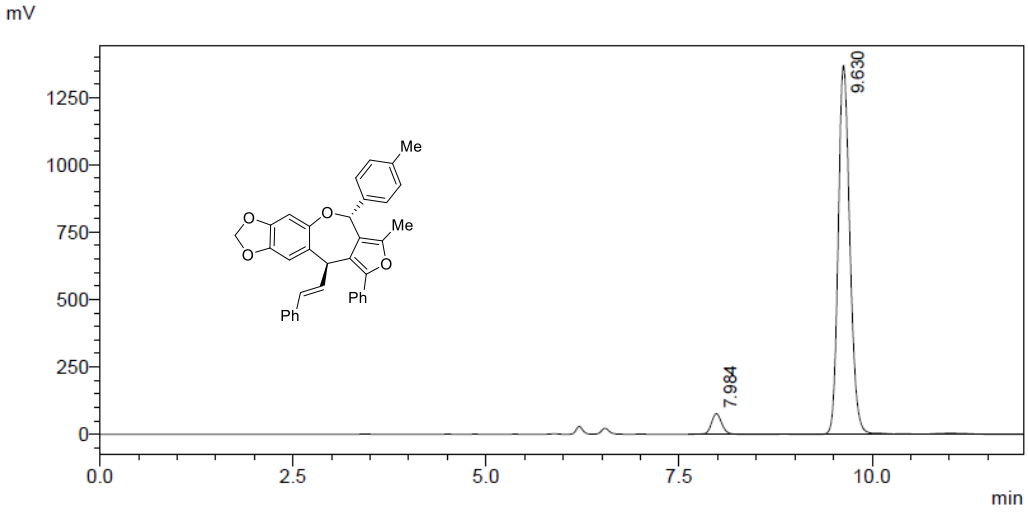


<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.999	1154705	129336	49.999
2	9.543	1154743	112377	50.001
		2309447	241713	100.000

<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.984	739000	76850	4.845
2	9.630	14513920	1367453	95.155
		15252919	1444303	100.000

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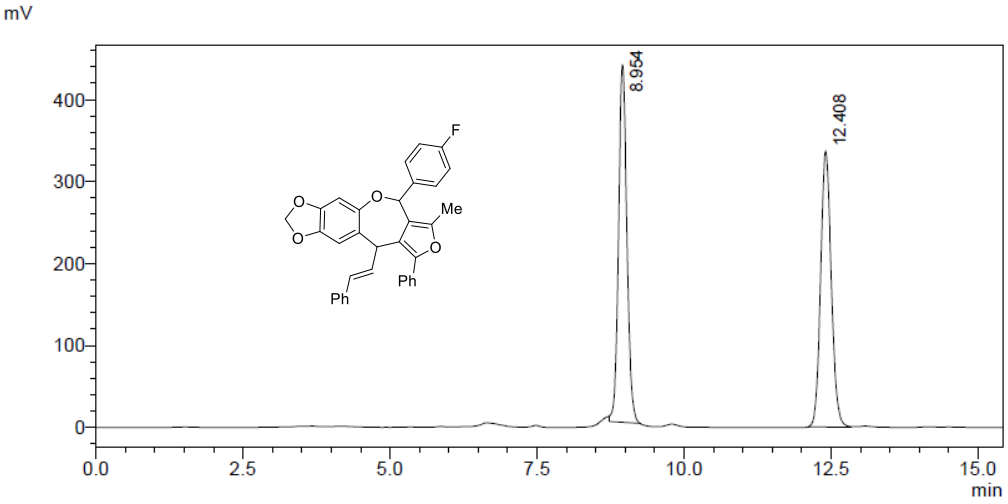

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	8.954	4297472	436192	50.351
2	12.408	4237629	336693	49.649
		8535100	772884	100.000

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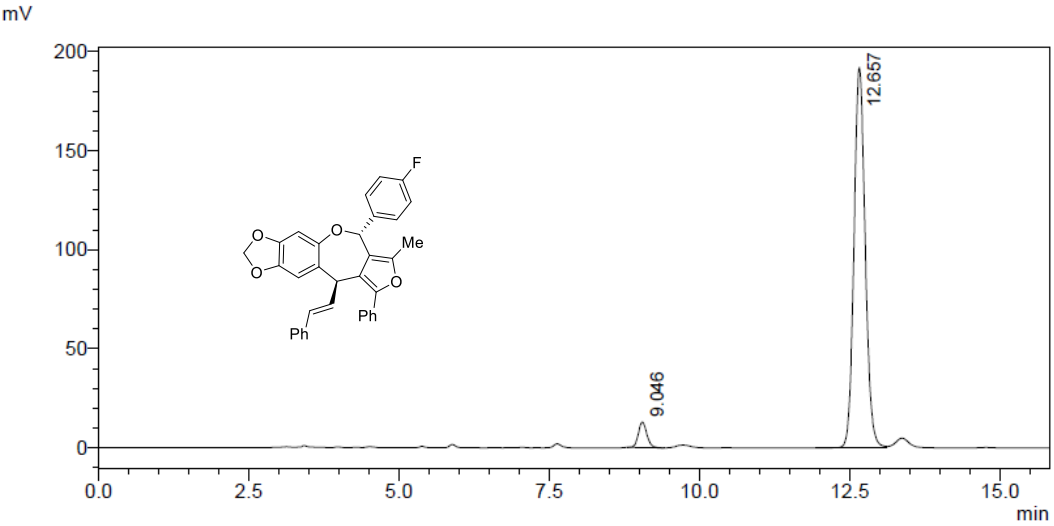

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	9.046	126755	12864	4.837
2	12.657	2493921	191907	95.163
		2620676	204771	100.000

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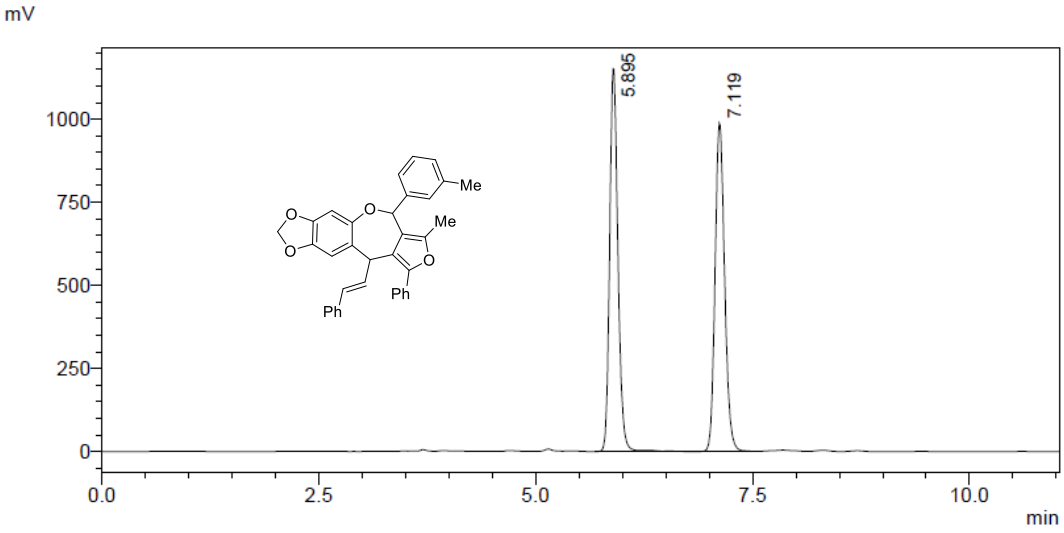

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.895	7673184	1152681	50.256
2	7.119	7594885	989179	49.744
		15268069	2141860	100.000

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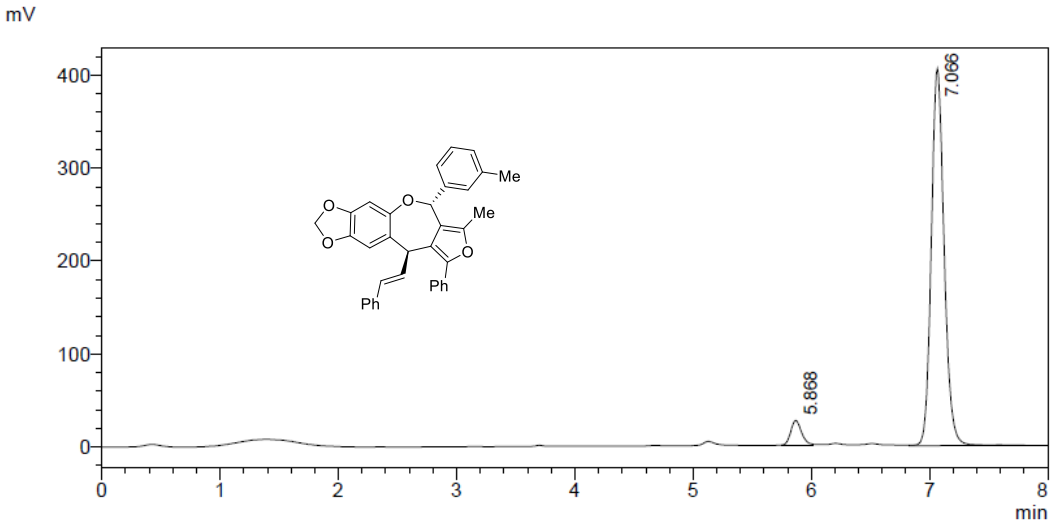

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.868	168163	26557	5.178
2	7.066	3079231	406006	94.822
		3247395	432563	100.000

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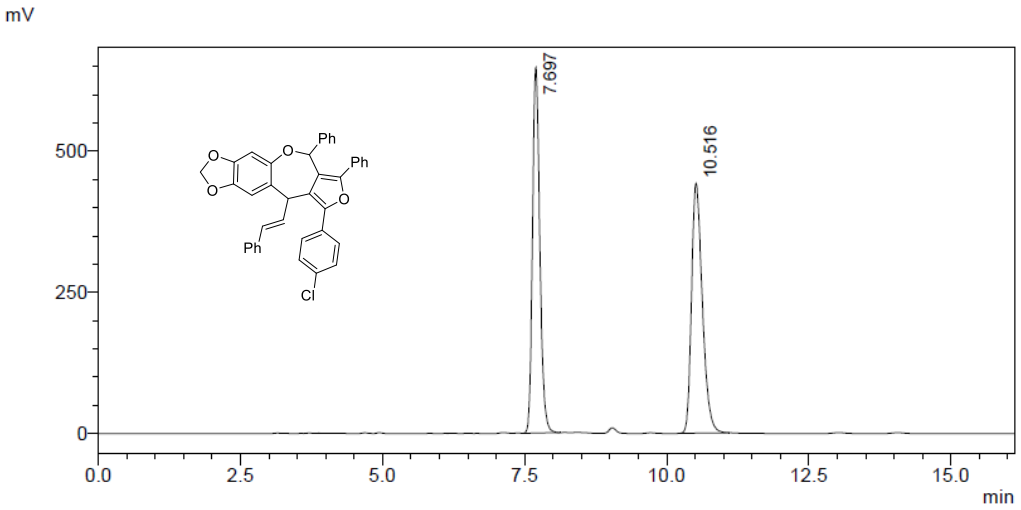

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.697	5807686	647932	49.804
2	10.516	5853407	442401	50.196
		11661093	1090333	100.000

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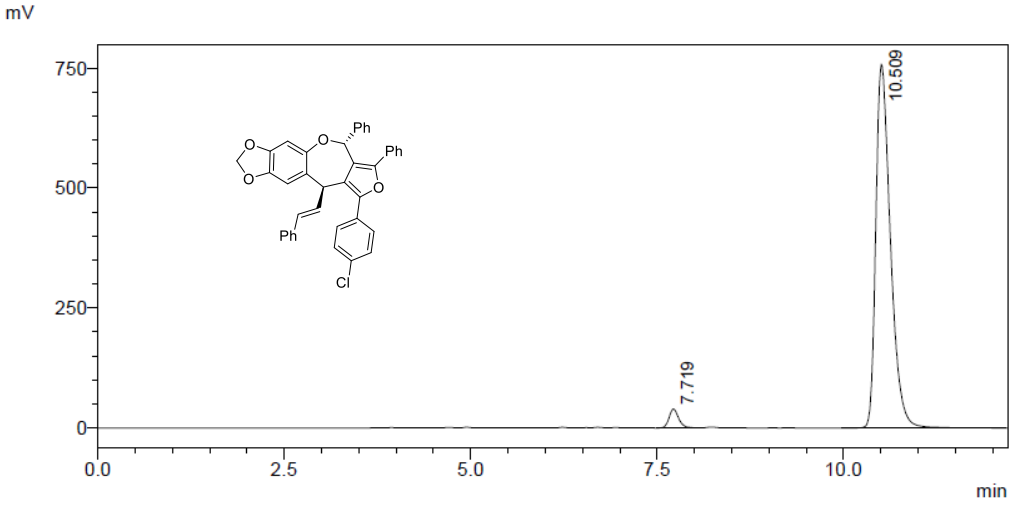

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.719	359841	39581	3.361
2	10.509	10345071	757251	96.639
		10704912	796831	100.000

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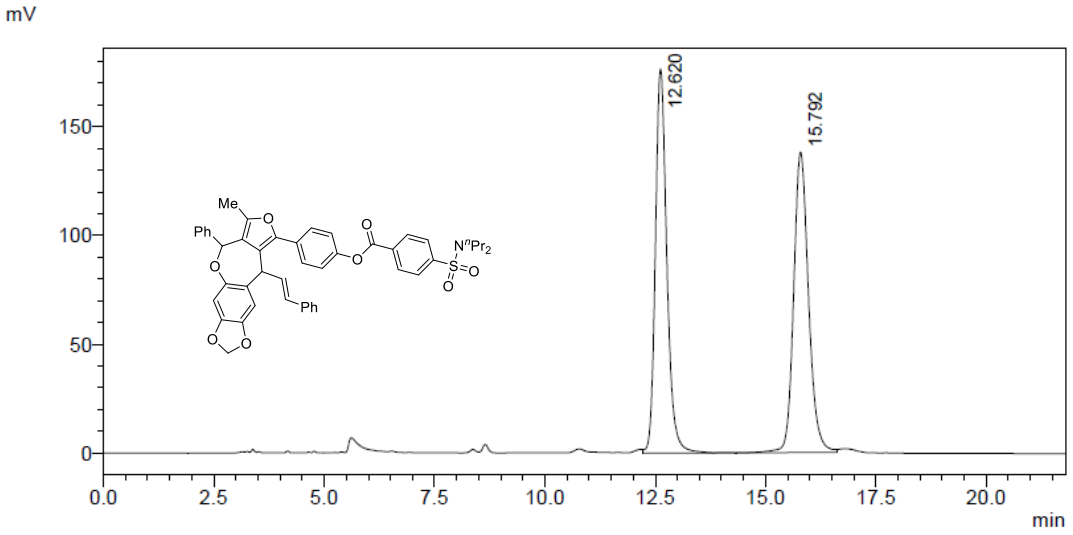

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	12.620	3190608	176417	49.622
2	15.792	3239240	137989	50.378
		6429848	314406	100.000

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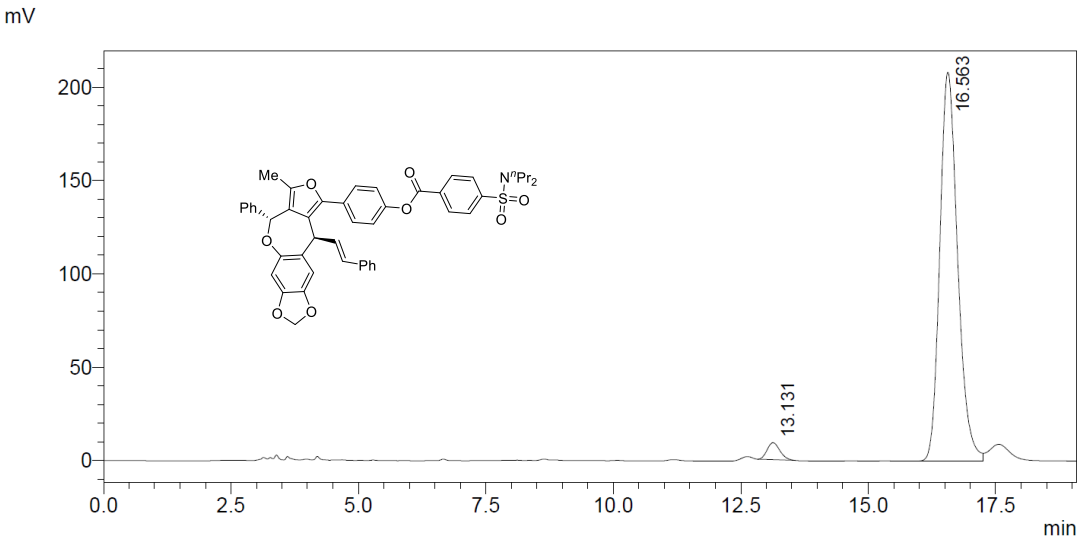

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	13.131	157324	9073	3.011
2	16.563	5067027	208257	96.989
		5224351	217330	100.000

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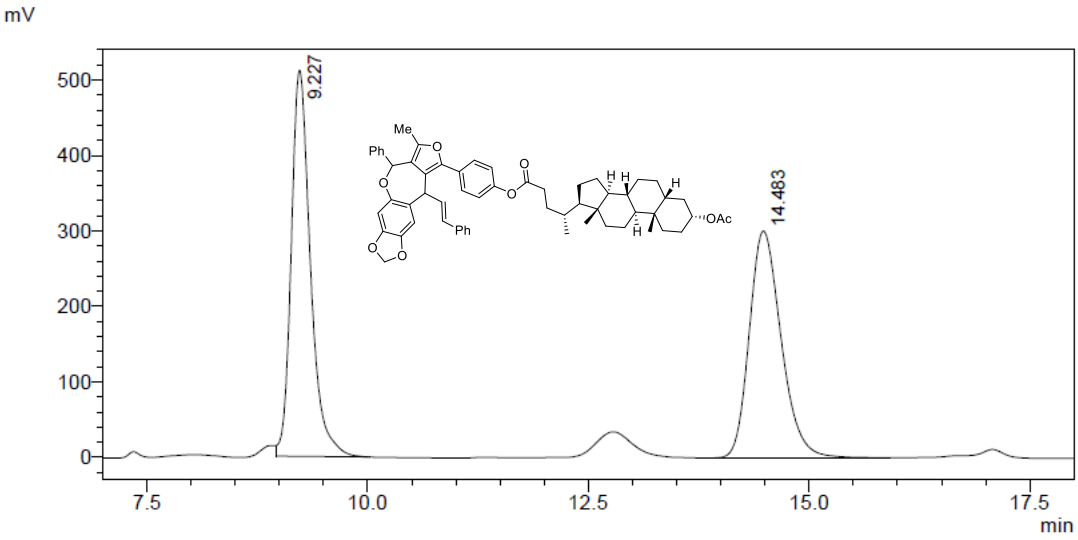

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	9.227	7745806	511640	50.412
2	14.483	7619052	301200	49.588
		15364857	812840	100.000

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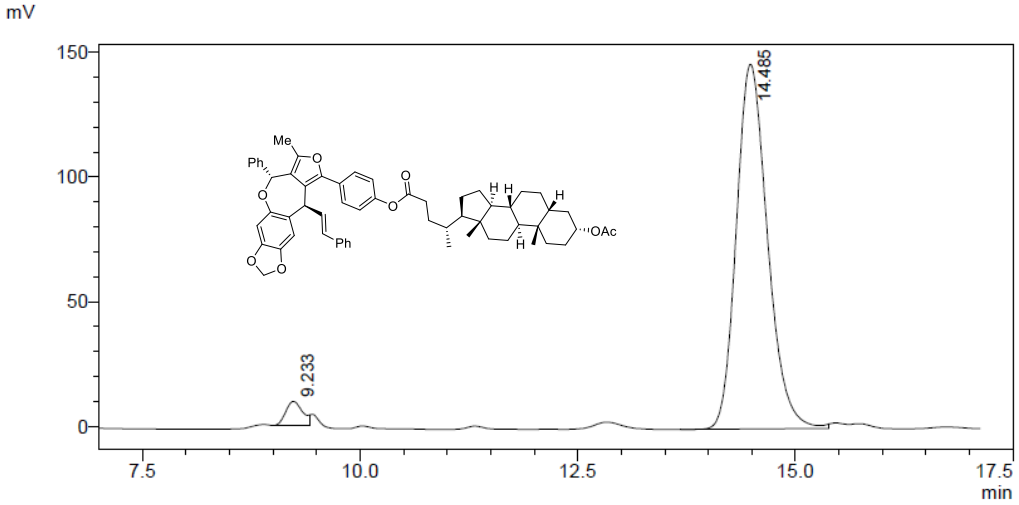

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	9.233	129080	9606	3.418
2	14.485	3646942	146239	96.582
		3776022	155845	100.000

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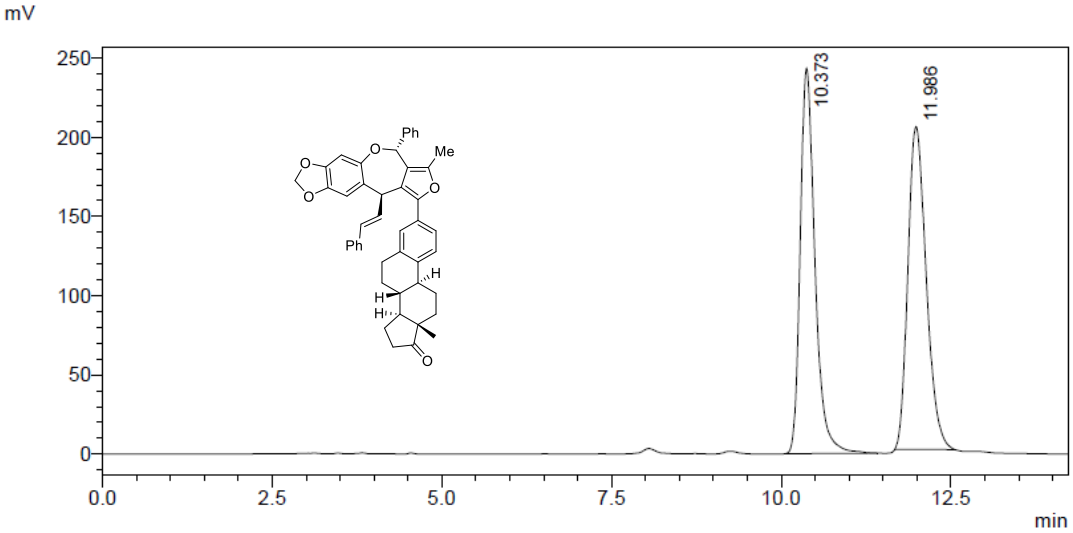

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	10.373	3679889	243453	49.009
2	11.986	3828677	203839	50.991
		7508566	447293	100.000

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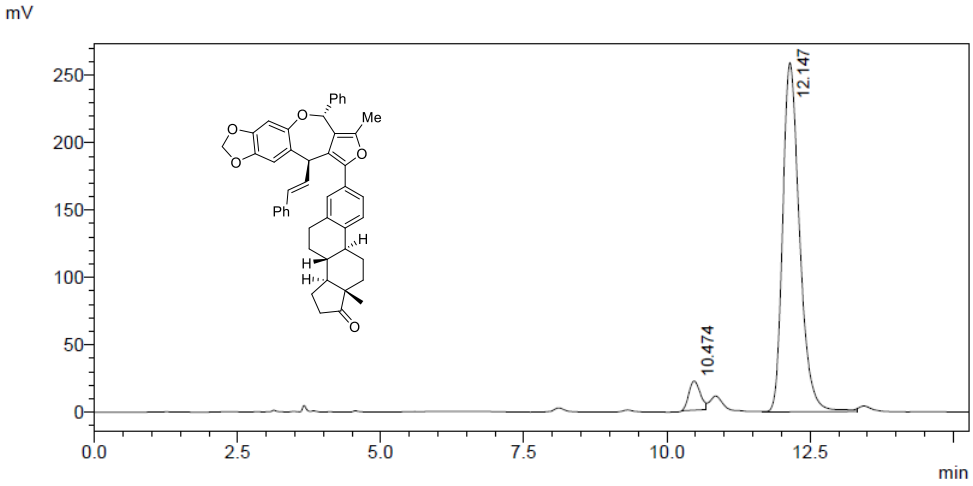
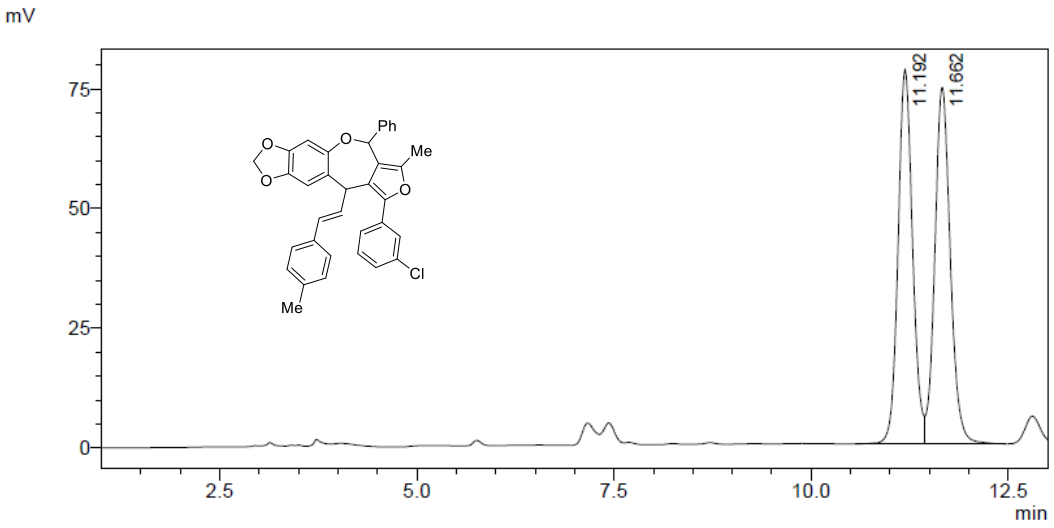


<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	10.474	300354	21678	5.341
2	12.147	5322739	259329	94.659
		5623093	281007	100.000

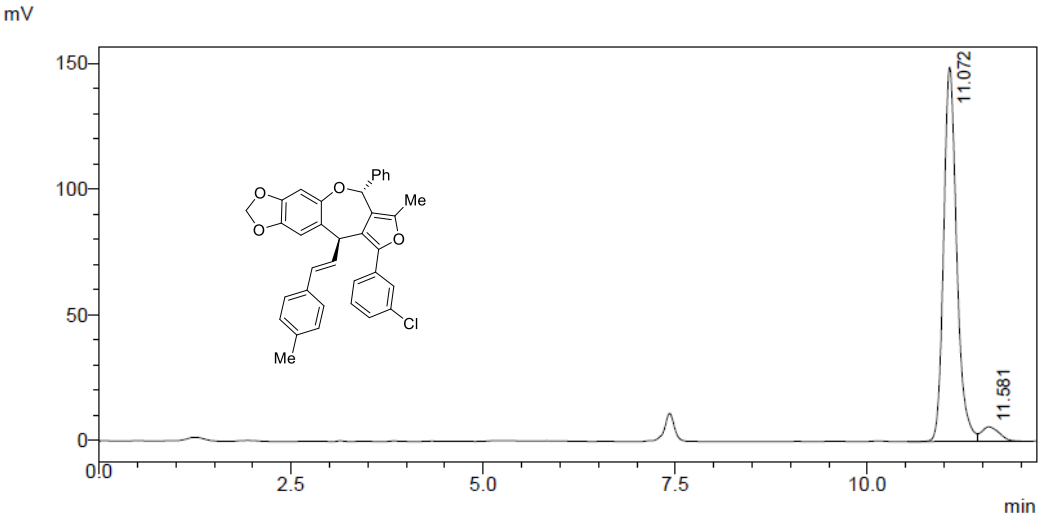
<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	11.192	1002644	78194	49.587
2	11.662	1019340	74417	50.413
		2021983	152611	100.000

<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	11.072	1768074	148813	94.993
2	11.581	93201	5721	5.007
		1861276	154534	100.000

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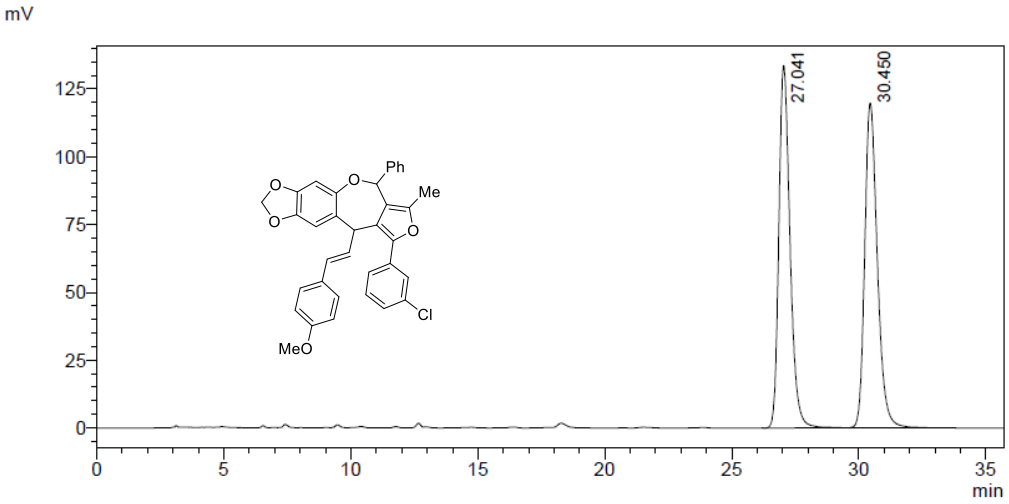

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	27.041	4093125	133628	49.738
2	30.450	4136171	119816	50.262
		8229296	253444	100.000

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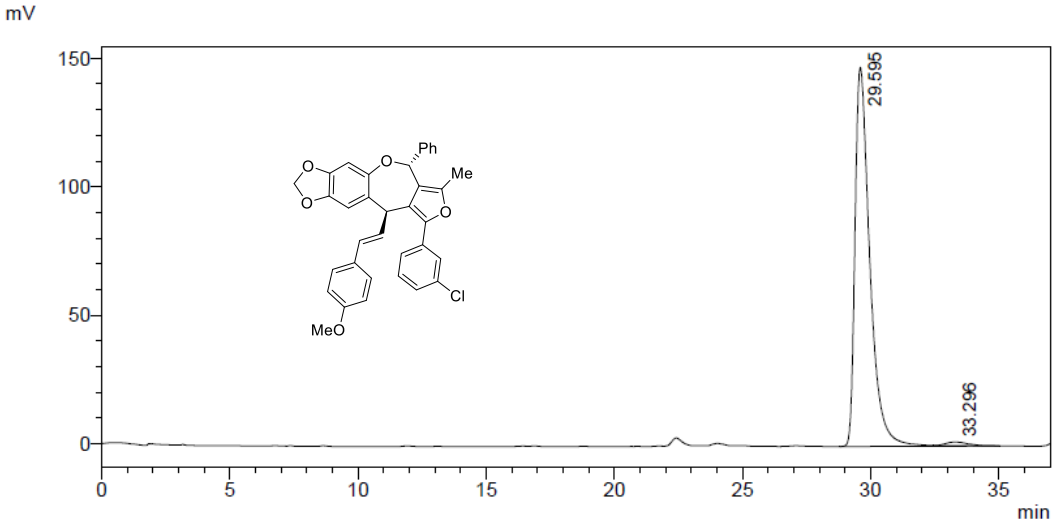

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	29.595	5952019	147558	98.636
2	33.296	82281	1407	1.364
		6034300	148965	100.000

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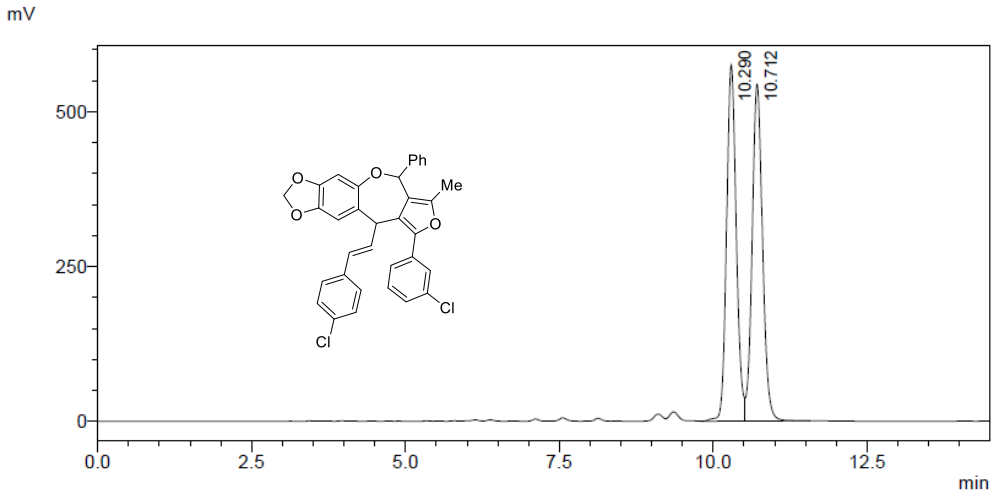
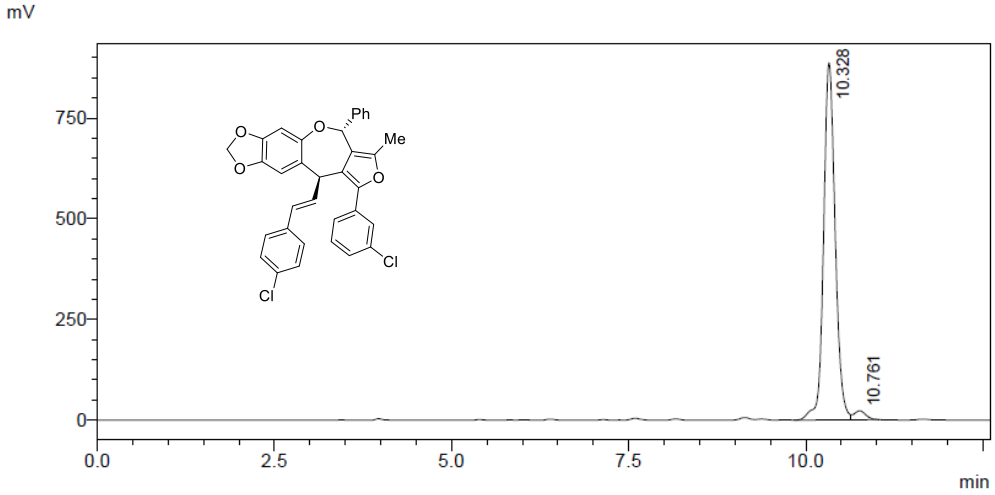


<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	10.290	6344073	575274	49.852
2	10.712	6381667	543896	50.148
		12725741	1119170	100.000

<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	10.328	10107223	886014	97.532
2	10.761	255745	22145	2.468
		10362968	908159	100.000

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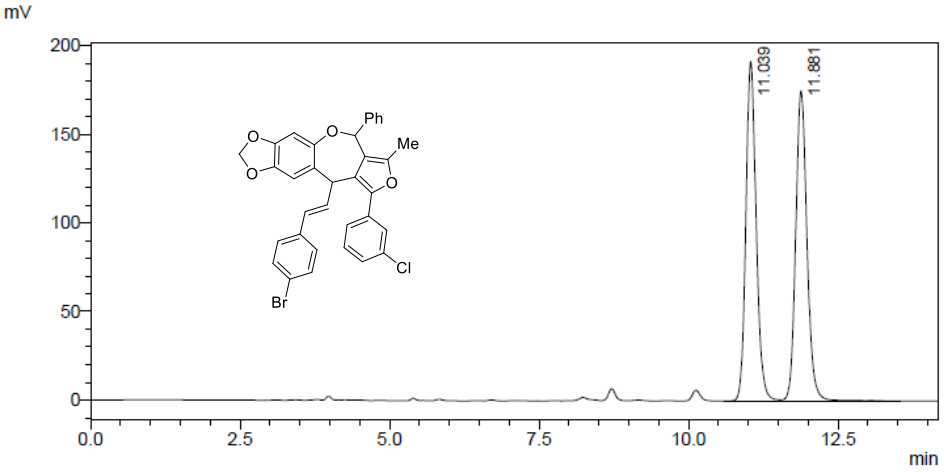

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	11.039	2298082	191317	50.011
2	11.881	2297100	174865	49.989
		4595182	366182	100.000

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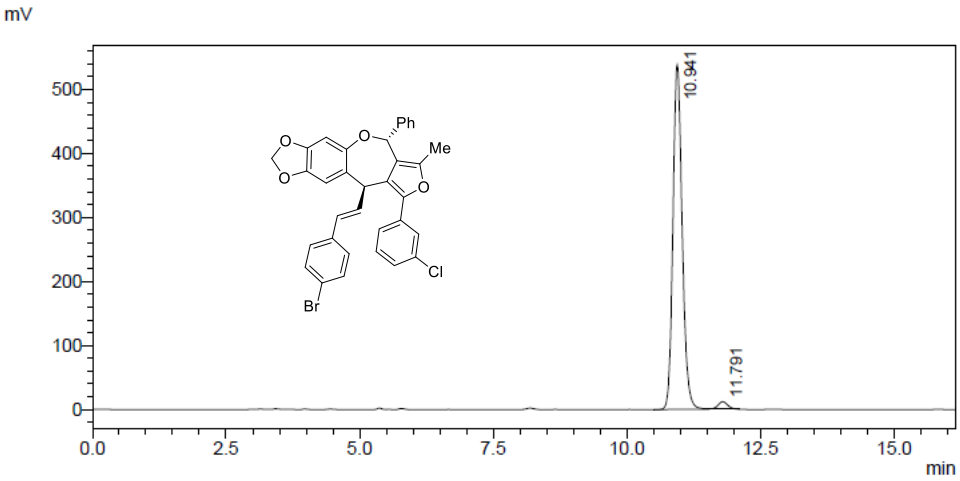

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	10.941	6484030	538540	97.677
2	11.791	154194	11935	2.323
		6638224	550476	100.000

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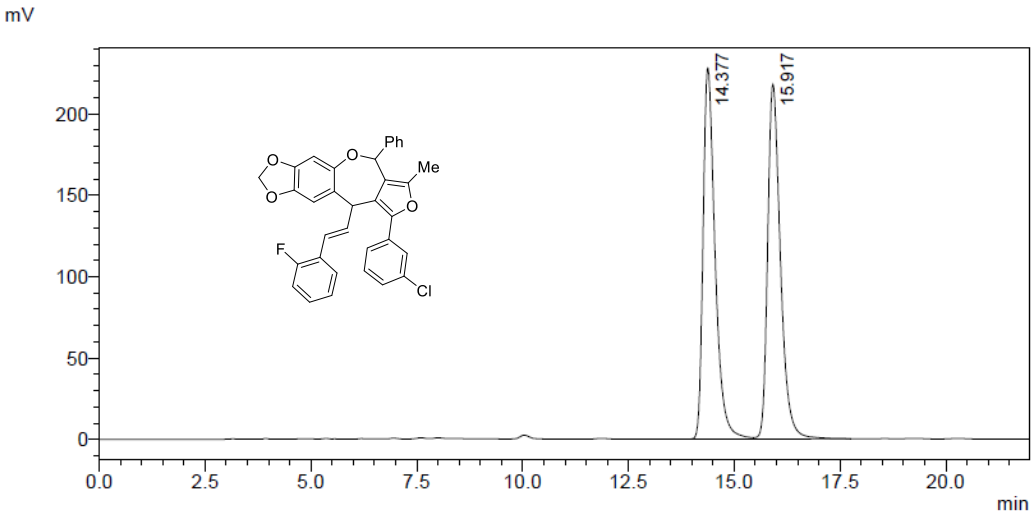
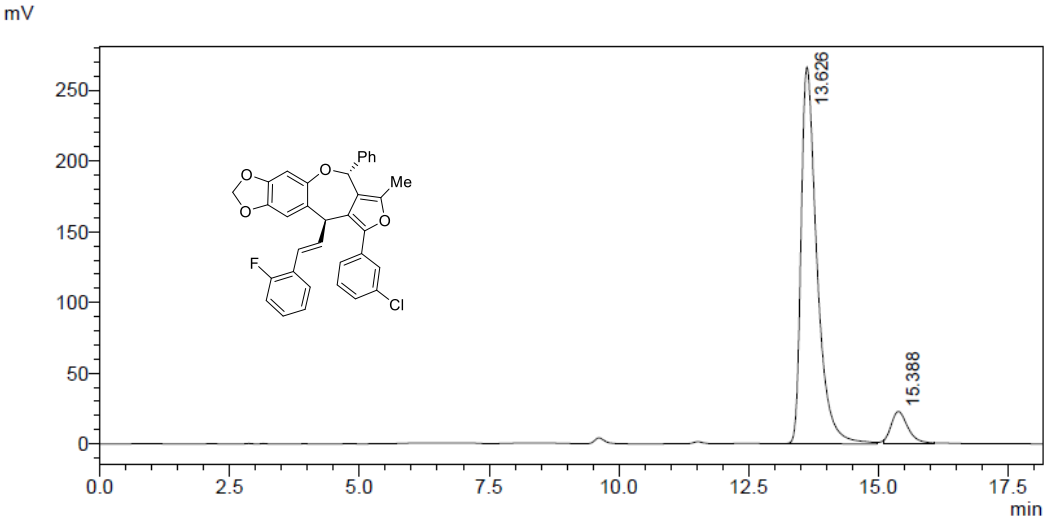


<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	14.377	4498470	227988	49.605
2	15.917	4570197	217773	50.395
		9068667	445761	100.000

<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	13.626	5663714	266222	91.845
2	15.388	502900	22500	8.155
		6166614	288722	100.000

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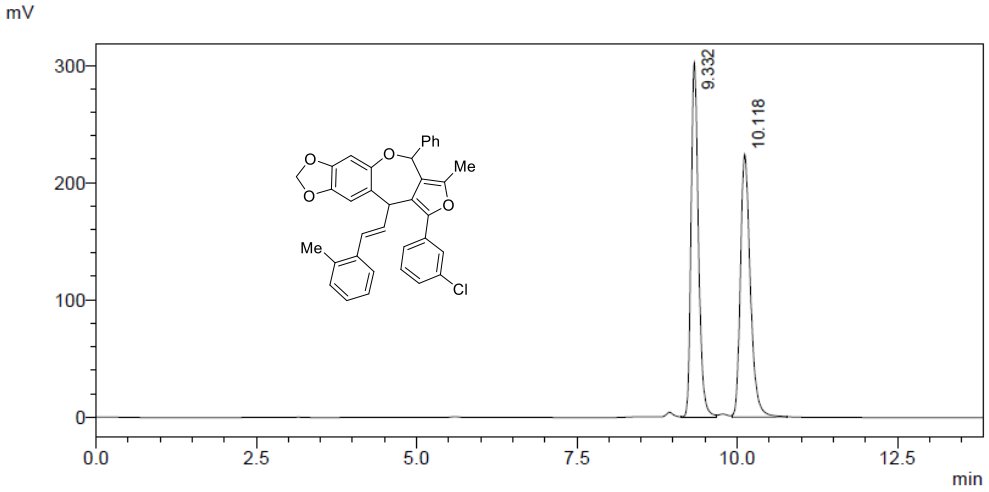
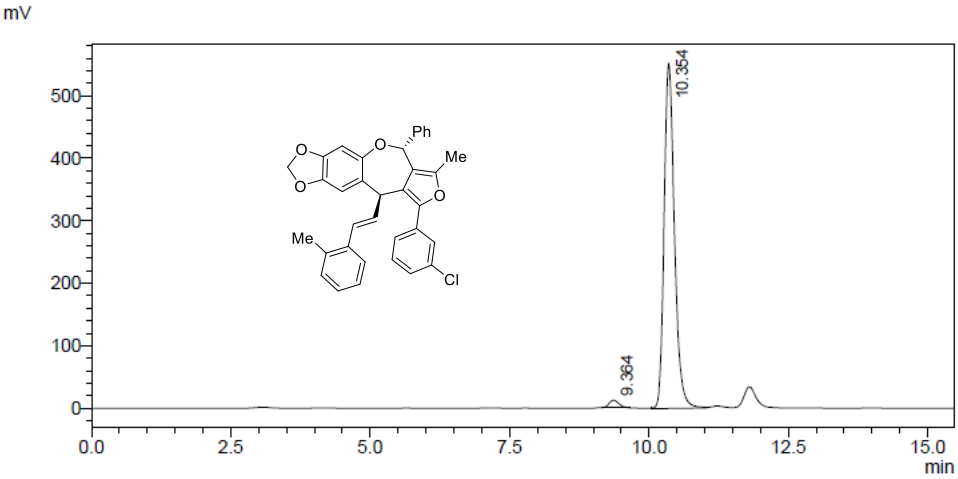


<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	9.332	2424854	301645	50.037
2	10.118	2421226	224047	49.963
		4846080	525692	100.000

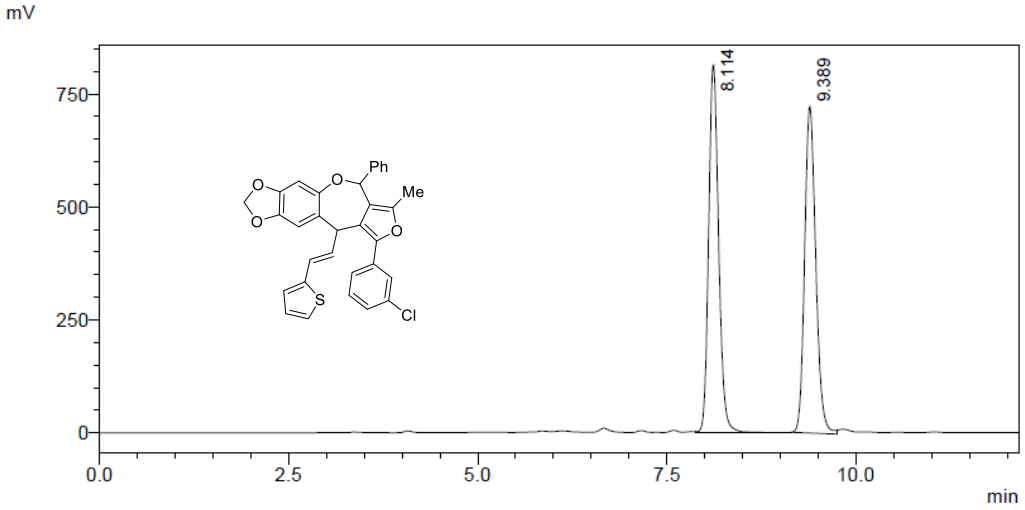
<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	9.364	157962	12416	2.171
2	10.354	7116714	551896	97.829
		7274676	564312	100.000

<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	8.114	7500932	814279	50.302
2	9.389	7410860	722892	49.698
		14911792	1537171	100.000

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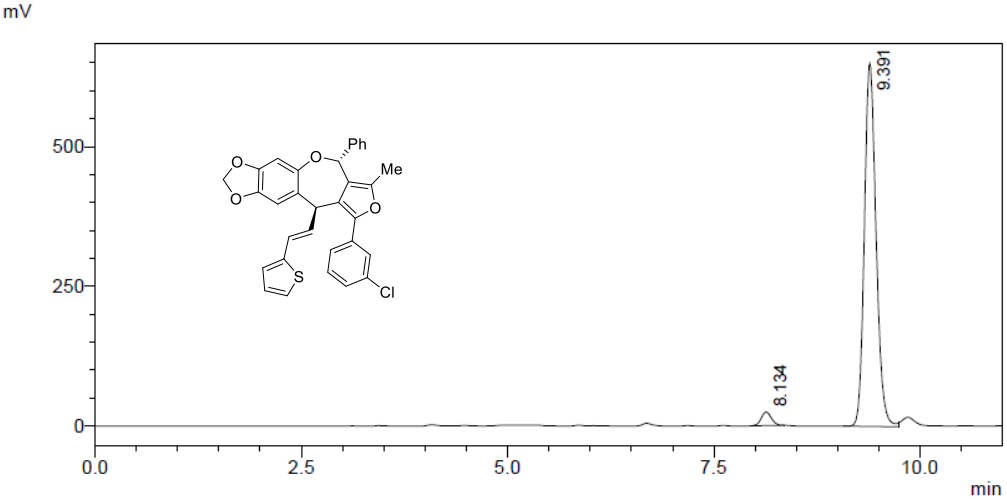
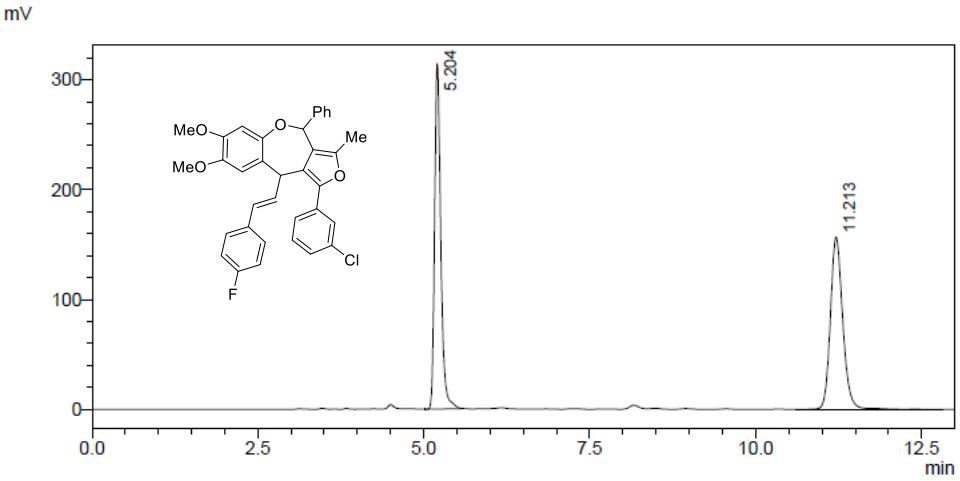


<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	8.134	206913	24257	3.127
2	9.391	6410983	650066	96.873
		6617896	674323	100.000

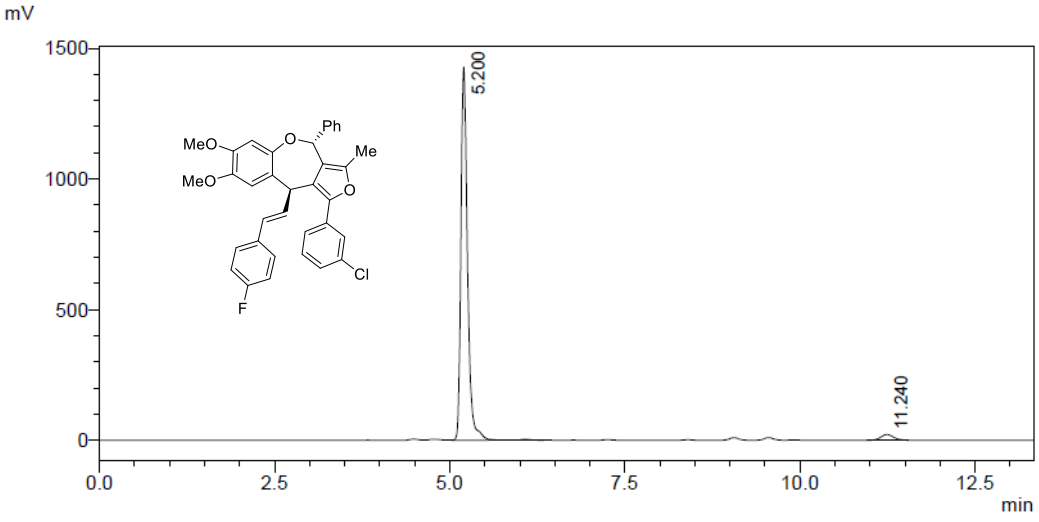
<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.204	2035729	313837	50.009
2	11.213	2035016	156657	49.991
		4070745	470494	100.000

<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.200	9350259	1430159	97.157
2	11.240	273577	21687	2.843
		9623836	1451846	100.000

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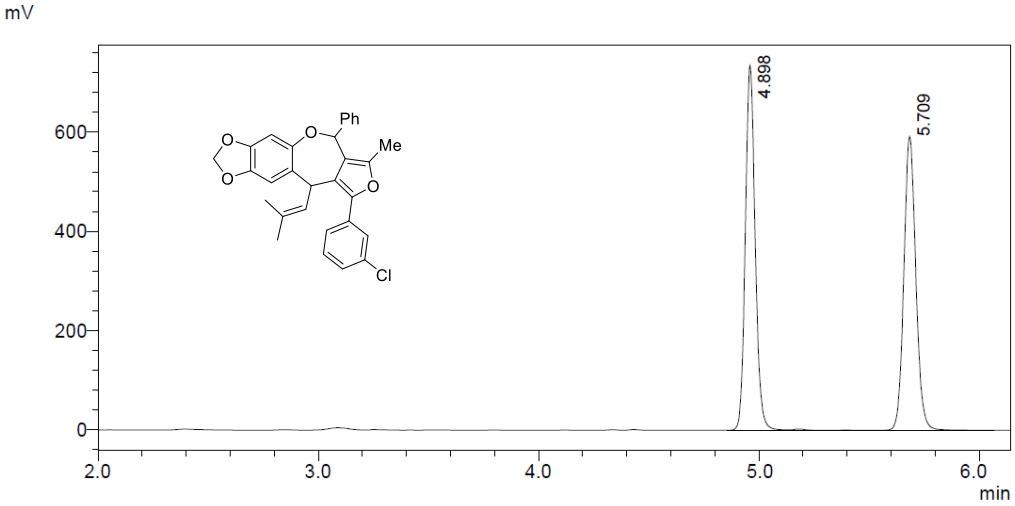
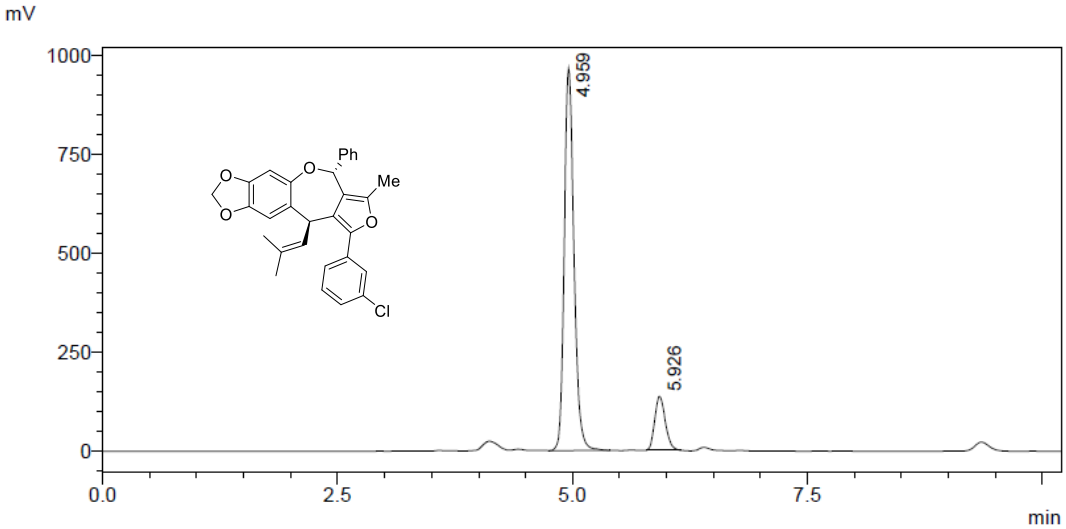


<Peak Table>

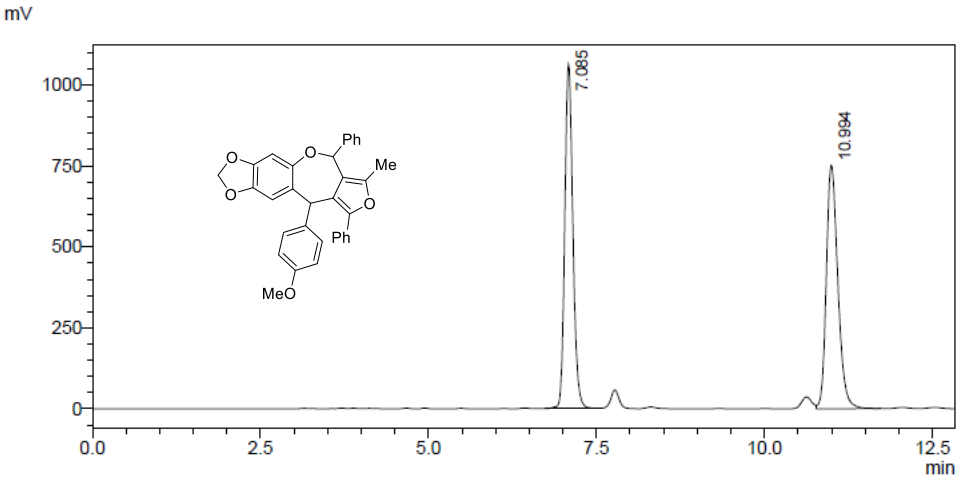
Peak#	Ret. Time	Area	Height	Area%
1	4.898	5738858	735416	50.640
2	5.709	5593799	592266	49.360
		11332657	1327682	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.959	6915750	964277	86.687
2	5.926	1062069	135755	13.313
		7977819	1100032	100.000

<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.085	8960371	1063437	50.003
2	10.994	8959404	751880	49.997
		17919775	1815316	100.000

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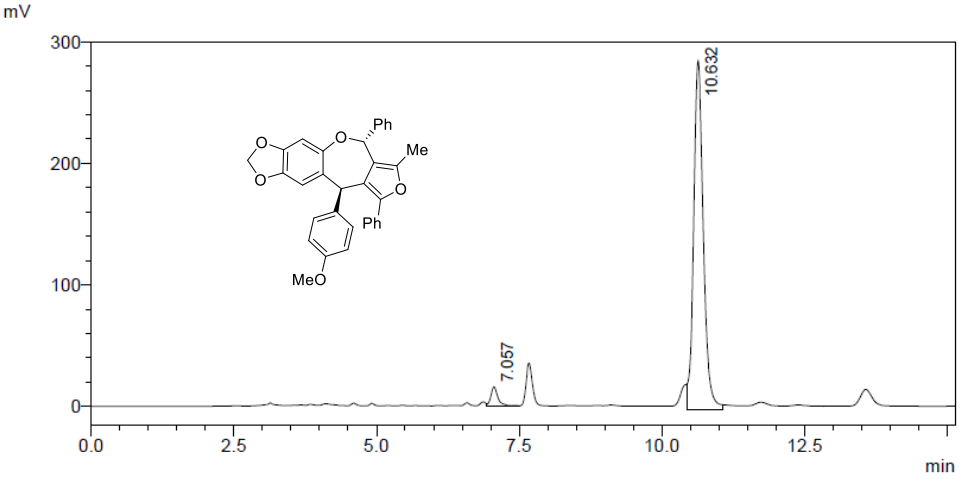

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.057	136908	15823	3.918
2	10.632	3357097	286611	96.082
		3494005	302434	100.000

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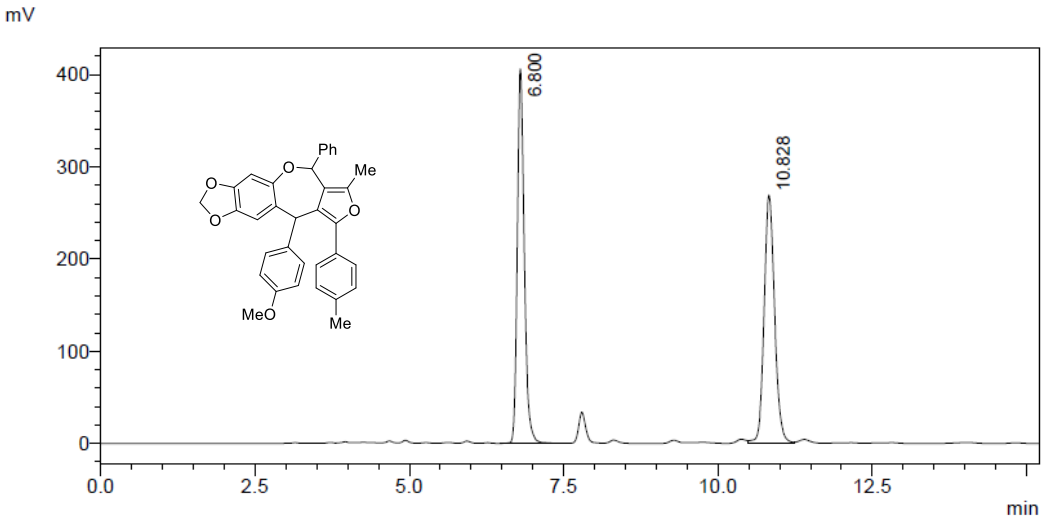
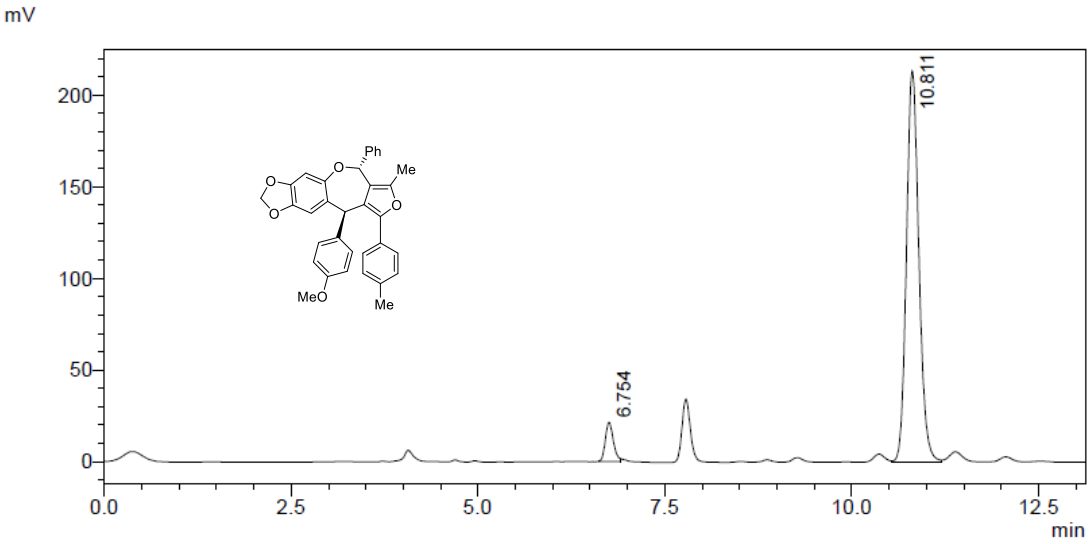


<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	6.800	3209234	406483	50.112
2	10.828	3194871	268842	49.888
		6404105	675326	100.000

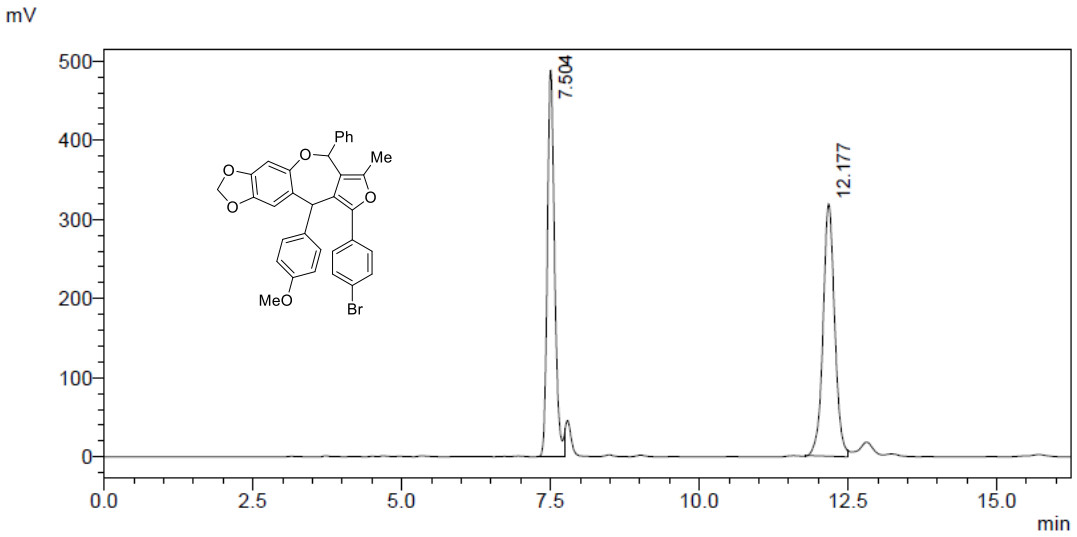
<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	6.754	161207	21347	6.117
2	10.811	2474259	213784	93.883
		2635466	235132	100.000

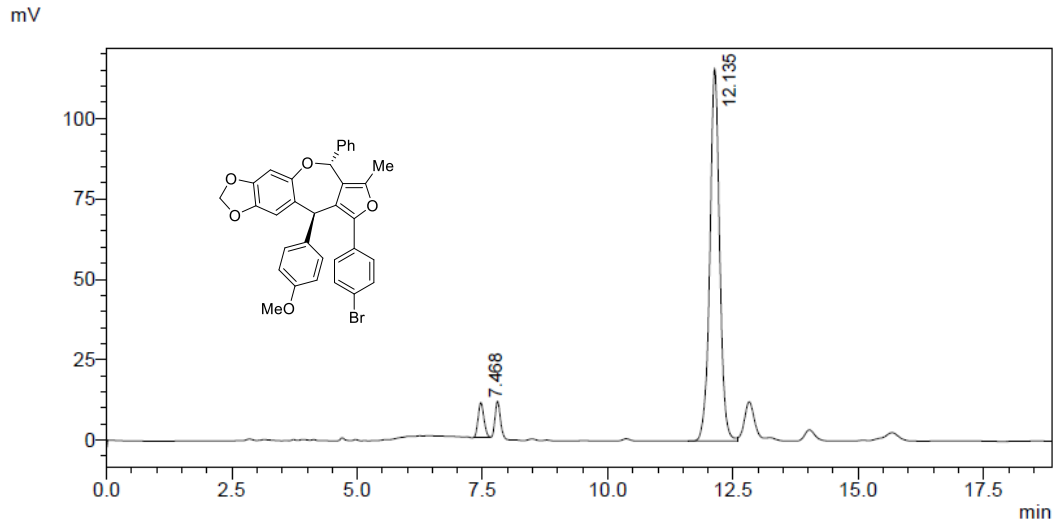
<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.504	4181710	487632	49.138
2	12.177	4328444	318800	50.862
		8510154	806432	100.000

<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.468	85880	10674	5.186
2	12.135	1570214	115617	94.814
		1656094	126291	100.000

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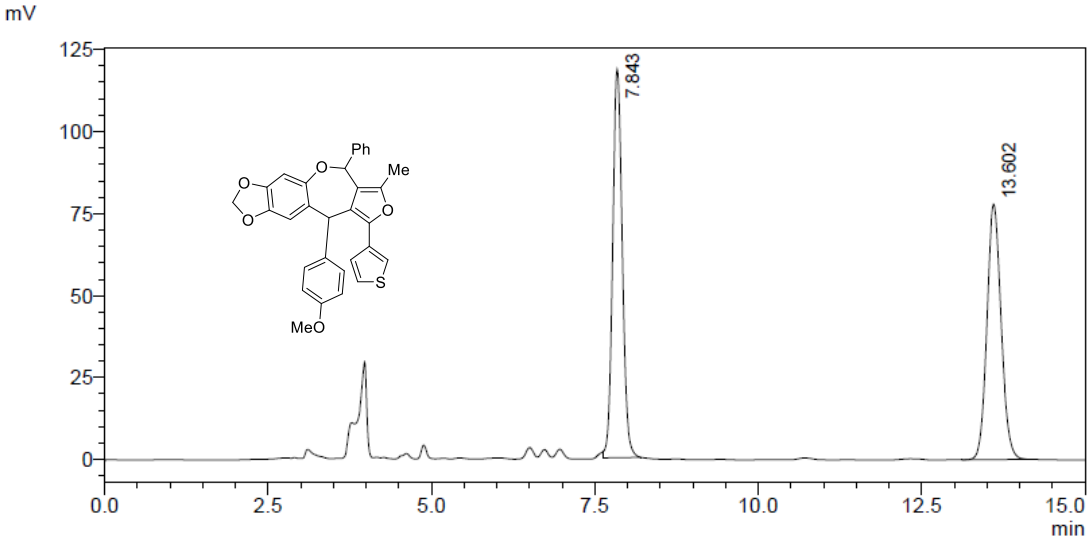
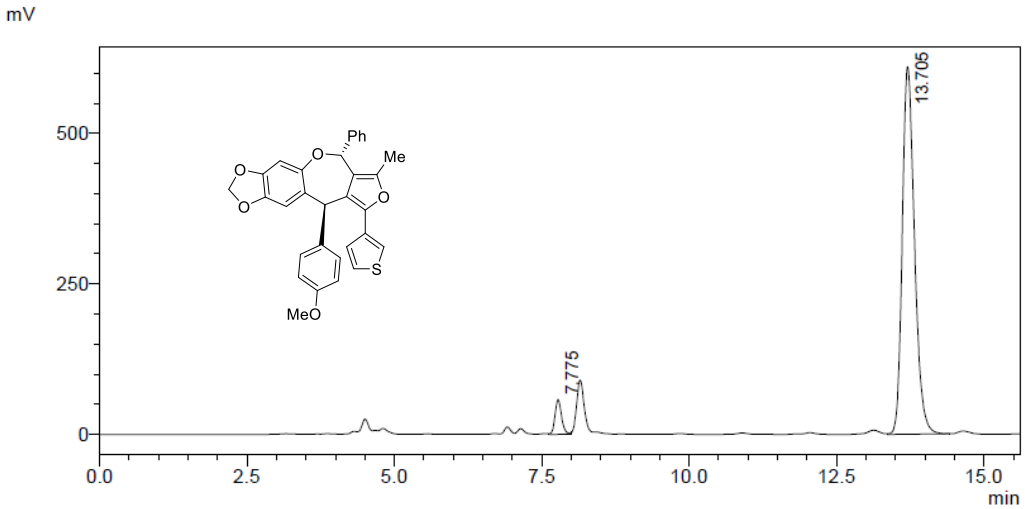


<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.843	1214102	118426	50.818
2	13.602	1175009	77820	49.182
		2389111	196246	100.000

<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.775	457358	57970	4.937
2	13.705	8806008	610216	95.063
		9263366	668186	100.000

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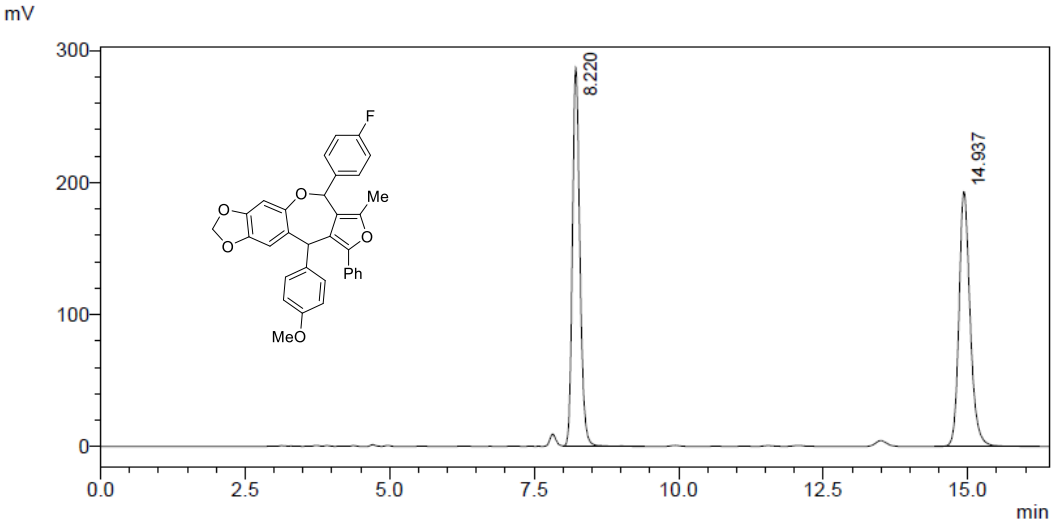

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	8.220	2593583	287004	50.005
2	14.937	2593077	193007	49.995
		5186660	480011	100.000

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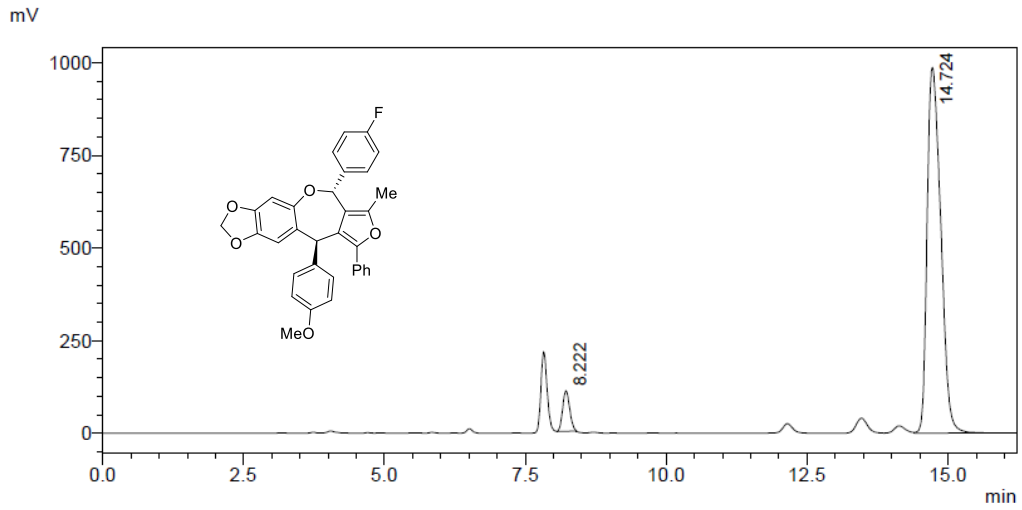

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	8.222	944896	108917	5.384
2	14.724	16606203	986828	94.616
		17551099	1095746	100.000

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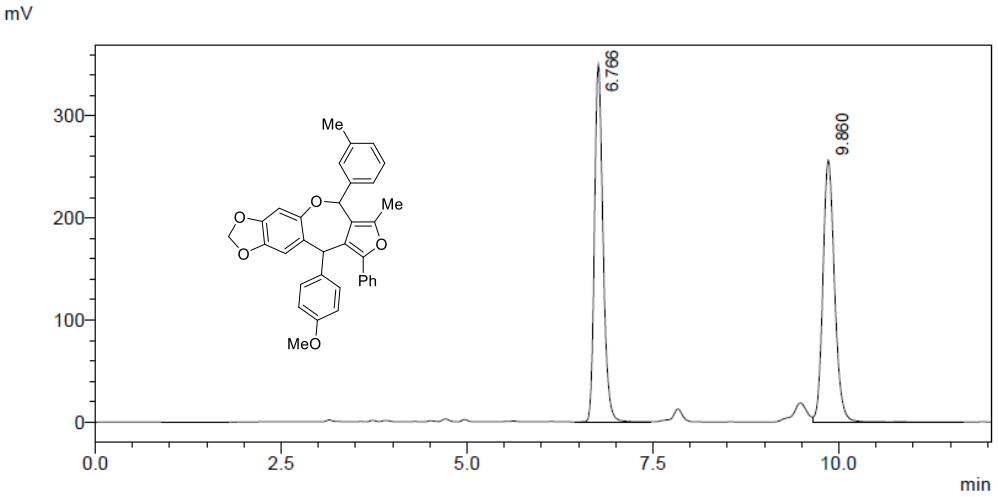

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	6.766	2810136	350134	50.029
2	9.860	2806910	256880	49.971
		5617046	607014	100.000

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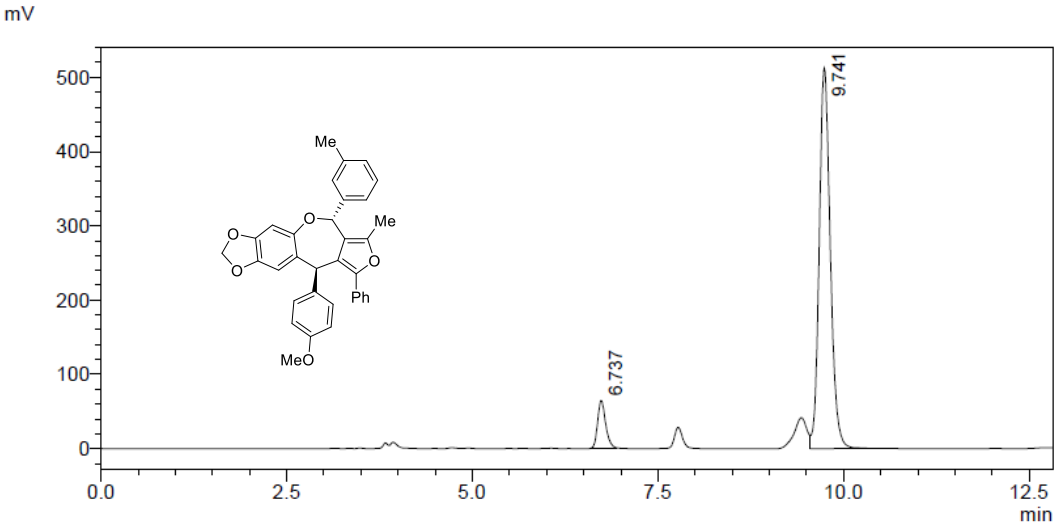

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	6.737	473164	63811	8.155
2	9.741	5329063	512672	91.845
		5802227	576483	100.000

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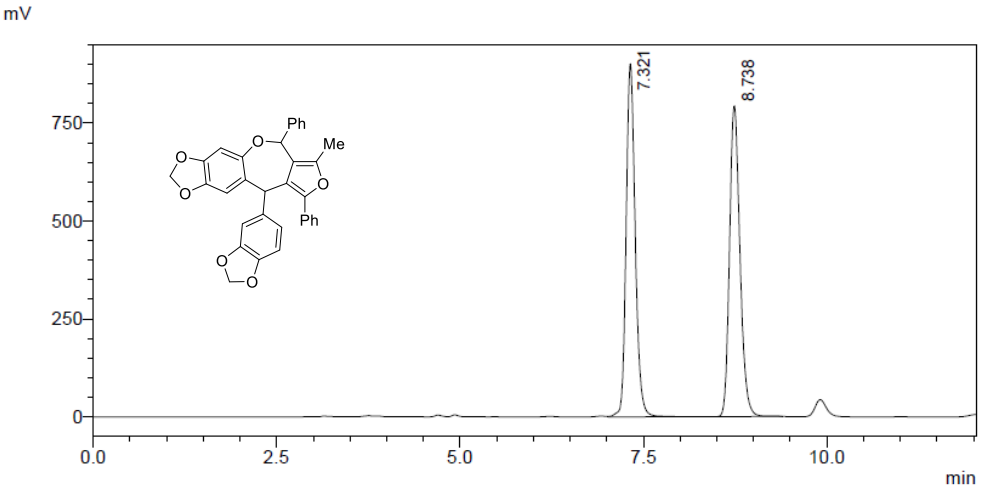

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.321	7782211	901068	49.751
2	8.738	7860017	792268	50.249
		15642227	1693336	100.000

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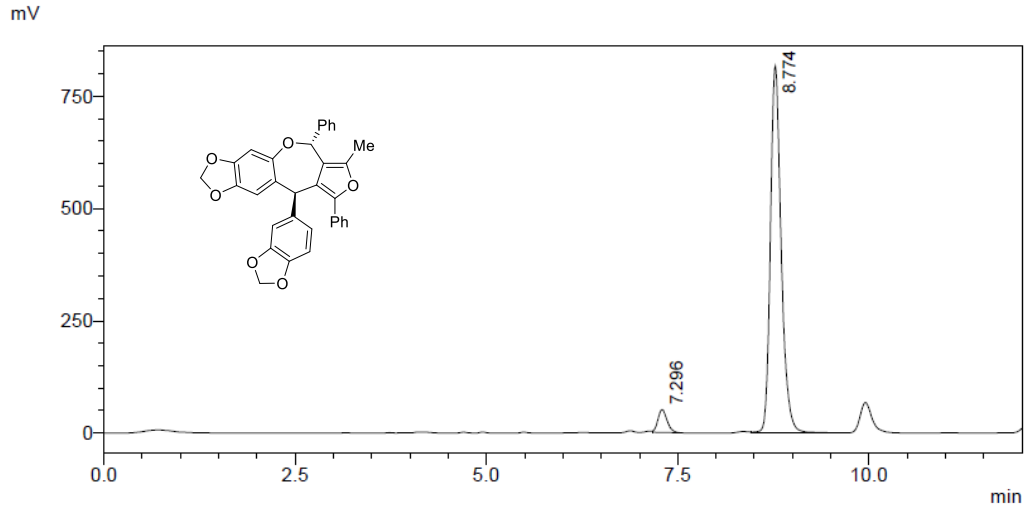

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.296	421775	50799	4.985
2	8.774	8039490	818112	95.015
		8461265	868911	100.000

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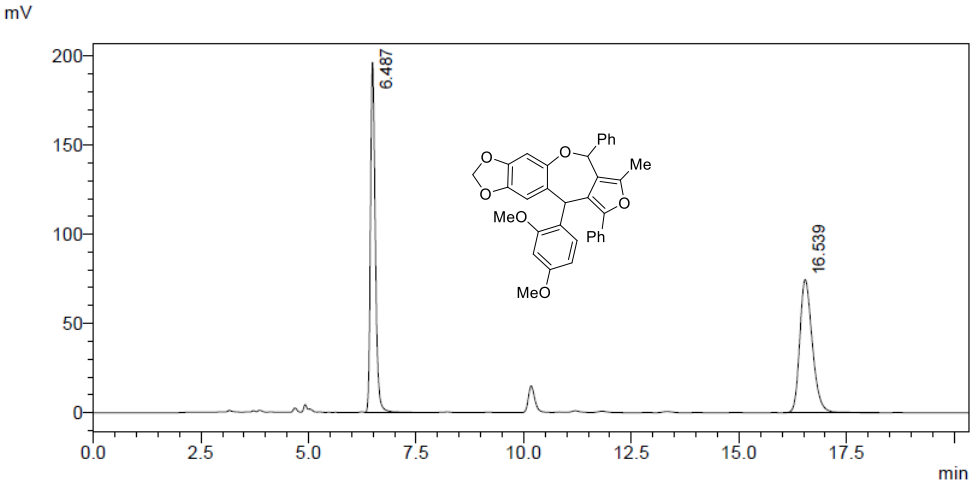

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	6.487	1538414	196070	50.291
2	16.539	1520608	74589	49.709
		3059022	270659	100.000

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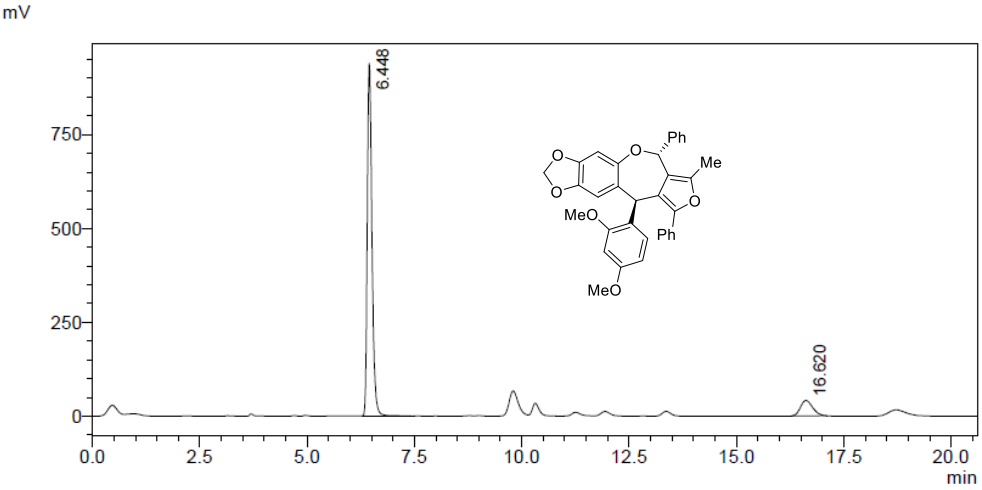

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	6.448	7158249	940314	89.860
2	16.620	807790	41162	10.140
		7966039	981477	100.000

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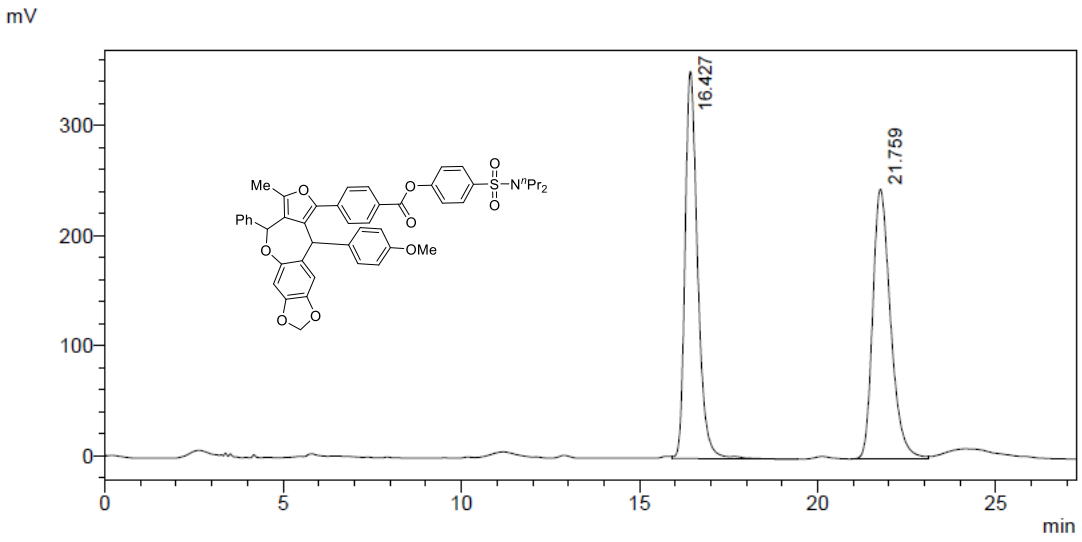

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	16.427	8598217	350995	50.147
2	21.759	8547796	244674	49.853
		17146013	595669	100.000

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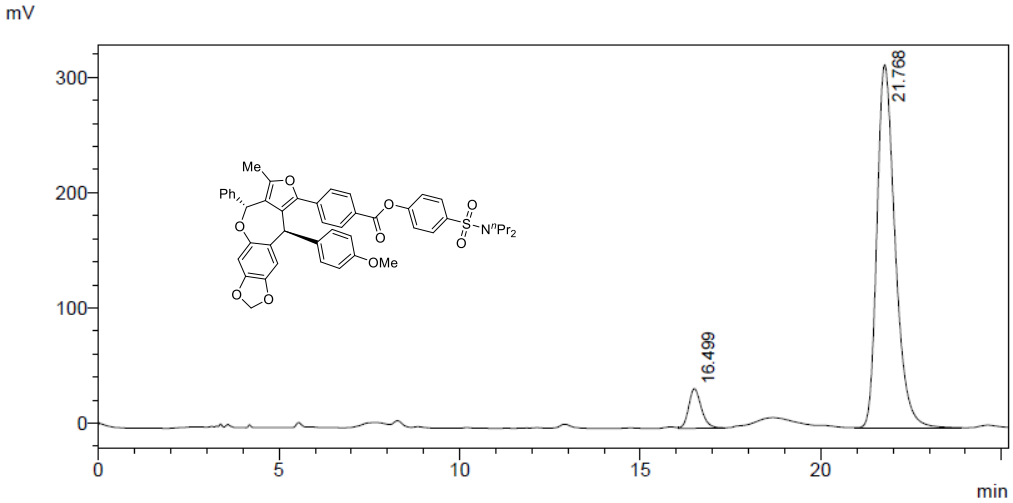
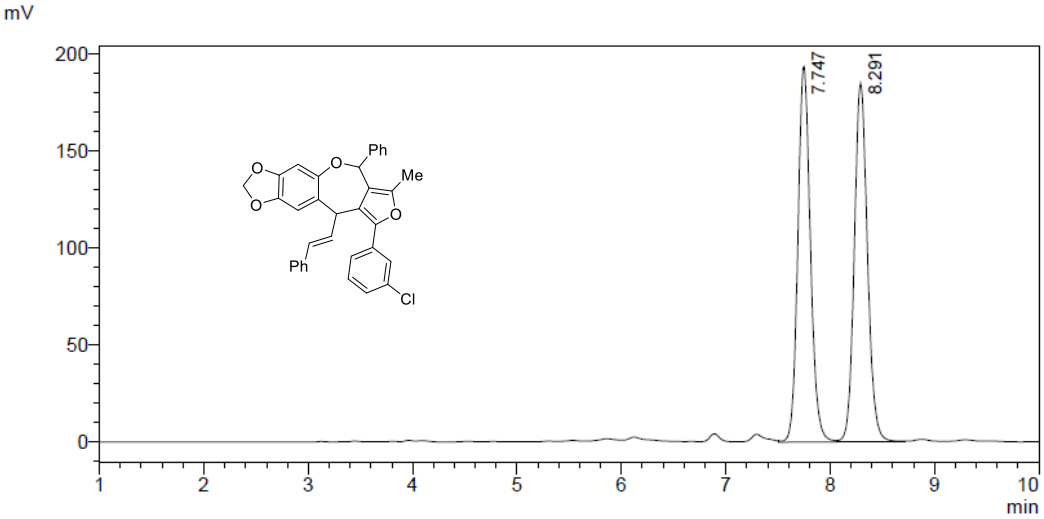


<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	16.499	844667	34389	7.137
2	21.768	10991151	315034	92.863
		11835818	349423	100.000

HPLC chromatograph of 3ja on large-scale synthesis

<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.747	1619090	193658	49.871
2	8.291	1627447	185043	50.129
		3246537	378701	100.000

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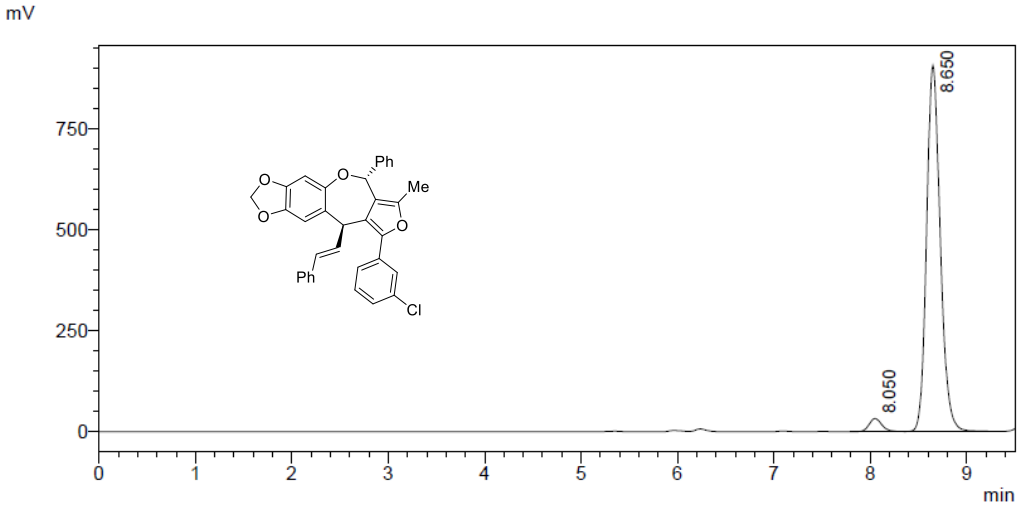
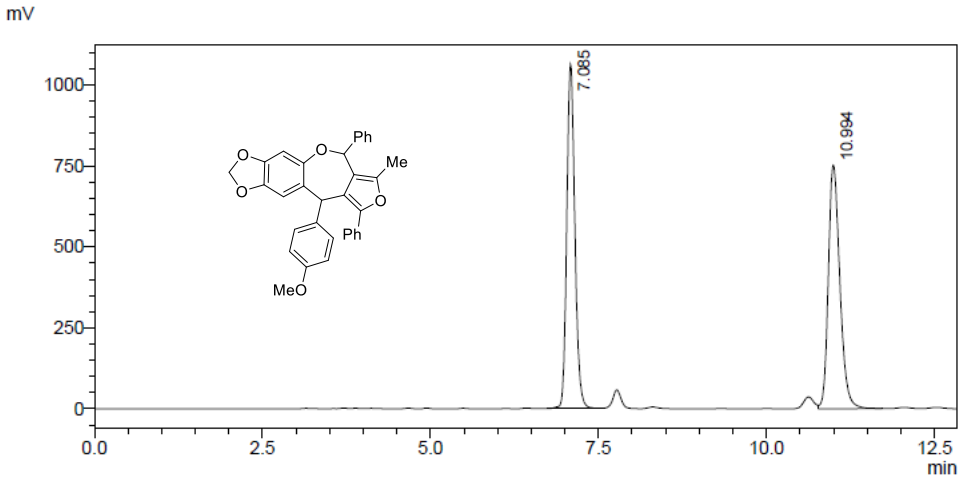


<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	8.050	309359	32789	3.328
2	8.650	8986950	906602	96.672
		9296309	939391	100.000

HPLC chromatograph of 3aj on large-scale synthesis

<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.085	8960371	1063437	50.003
2	10.994	8959404	751880	49.997
		17919775	1815316	100.000

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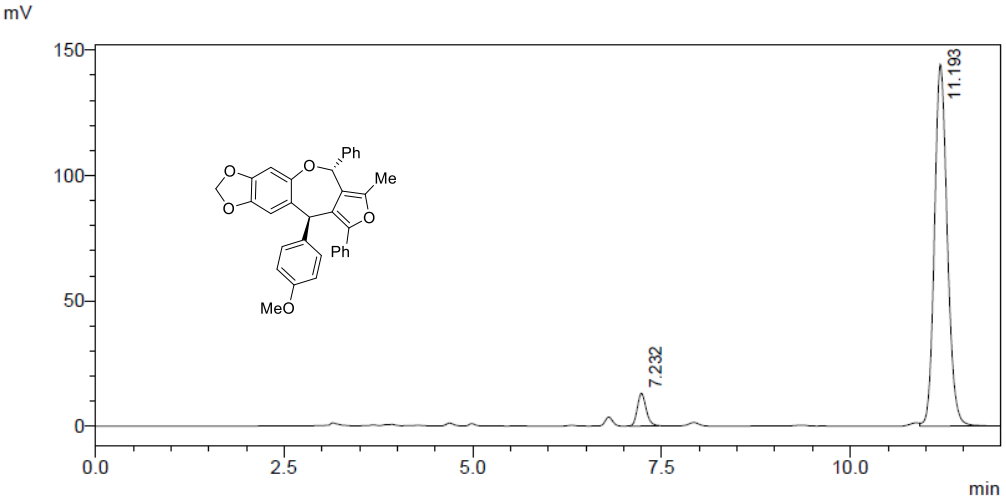

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.232	106001	13051	5.846
2	11.193	1707163	144311	94.154
		1813164	157363	100.000